THE PROBLEM OF ACID MINE DRAINAGE IN THE PROVINCE OF ONTARIO

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THE PROBLEM
OF
ACID MINE DRAINAGE
IN THE
PROVINCE OF ONTARIO

by

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INTRODUCTION

"I have reason to believe (that) there are good coals (here) also for I have observ'd (that) the runs of water have the same colour as that which proceeds from the coal mines in Wales".

Written in 1698, the above statement is believed to be one of the first actual references made in North America to the problem that we know as 'acid mine drainage'.

The problem of acid mine drainage is not confined to North America alone. The naturally-occurring acid mine drainage reactions generate amber and yellow-tinted waste flows in coal and sulphide mining camps around the world.

In the not-too-distant past, severe acid mine drainage problems were thought to occur only as a result of coal mining operations. Since coal has never been mined to any significant extent in the Province of Ontario, acid mine drainage problems were not expected. However, in 1967, the Ontario Water Resources Commission correctly identified acid mine drainage as a major environmental problem in the hardrock uranium mining district of Elliot Lake, Ontario. Subsequently the problem was noted in the copper-lead-zinc camp at Manitouwadge, the nickel camp at Sudbury and at numerous isolated base metal properties both within and outside of the Province of Ontario.

This report is intended solely for information purposes. Its' prime function is to provide, in a single document, enough detailed information concerning various aspects of the problem of acid mine drainage in the Province of Ontario to enable a reader in Ontario to at least grasp the fundamental concepts (the causes, the effects, the cures) of acid mine drainage problems.

Under no circumstances should this report be regarded as an attempt to bring together all known information concerning the problem of acid mine drainage. In some respects, the acid mine drainage problems of the coal producing regions of the world are very similar to the acid mine drainage problems that arise from the recovery of sulphide or sulphide-associated ores. In other respects, however, the problems are significantly different. As a result, this report places great emphasis on factors that apply, in particular, to the hardrock sulphide mining industry.

SUMMARY

In general, this report provides enough information in each of its thirty sections to enable a reader to individually arrive at accurate conclusions regarding various aspects of the problem of acid mine drainage in the Province of Ontario. As a result, a summary of very specific conclusions is not presented in this report. There are, however, some basic conclusions that are either stated or implied in the report. These conclusions are as follows:

(1) The problem of acid mine drainage is common in the sulphide mining camps of the Province of Ontario.

(2) The factors that contribute to the problem of acid mine drainage vary in number and extent from property to property. For this reason, the solution to any particular problem of acid mine drainage depends largely on local circumstances. Important factors include:

- (i) the chemical composition of the rock mass being mined
- (ii) the geography of the property
- (iii) the mine-mill circuit being used
- (iv) solid and liquid waste disposal practices
- (v) the size, location, destination, use and chemical characteristics of the receiving watercourse

(3) Acid mine drainage problems occurring in the Province of Ontario are a result of the decomposition of the iron sulphide minerals pyrite, pyrrhotite and marcasite.

(4) Acid mine drainage problems can continue at a property long after the property has been abandoned.

(5) Conventional mine-mill waste treatment techniques vary greatly in effectiveness. However, it appears that even the most effective techniques cannot, by themselves, achieve a product that is completely acceptable for discharge to a natural watercourse.

(6) Three basic waste treatment oriented techniques should be considered at every property where acid mine drainage problems are existent or expected. These techniques are:

   (i) mine-mill wastewater re-use

   (ii) gangue sulphide recovery

   (iii) revegetation of abandoned or unused areas

A GENERAL LOOK AT SULPHIDE MINING

In mining the term 'hard rock' is loosely used to distinguish igneous and metamorphic rocks from sedimentary rocks. The Canadian Shield, a vast Precambrian complex, is one of the largest and richest hard-rock mining areas in the world. Thousands of square miles of Shield area lie within the boundaries of the Canadian Province of Ontario.

Mining operations on the Shield follow two basic patterns: - open pit and conventional underground. Of the two, underground operations predominate. It is not unusual, however, for open pit mining to precede conventional underground mining at any particular deposit providing that the geology and ground conditions are suitable.

There are standard underground mining procedures but the varying shapes of orebodies and changeable geology result in no two mines ever being alike.

Mines range all the way from the early prospect which may have only a single level with limited lateral workings to the deep and complex workings of mines that have been in production for many years. At the Dome Mine in the Porcupine area, for instance, there are about 130 miles of workings extending to a depth of one mile.

Opening and developing a mine is expensive. Shaft sinking costs approximate $300 per foot for a modest three-compartment shaft while drifting costs run to the order of $50 per foot. Consequently, any mine layout requires a great deal of planning. As it is desirable to obtain as much information as possible about the nature and attitude of the orebodies before shaft sinking commences, most mining companies like to carry out detailed drilling prior to launching any underground program.

Ore Reserves Defined

Ore is generally defined as a valuable mineral or an aggregate of valuable minerals, more or less mixed with a gangue (waste) material which from the standpoint of a miner can be won at a profit or from the standpoint of the metallurgist can be treated at a profit. Thus, in the case of a mineral-bearing vein, if the average value of a sufficient tonnage is such that a profit is indicated, then the vein filling is called ore. Otherwise, the vein filling is just waste rock.

An ore body is generally a solid and fairly continuous mass of ore which may include low-grade and waste as well as pay ore but is individualized by form or character from adjoining country rock.

Positive ore is ore which is exposed and properly sampled on four sides, in blocks of a reasonable size, having in view the nature of the deposit as regards uniformity of value per ton and of the third dimension, or thickness.

Proven ore is therefore ore involving practically no risk of failure of continuity.

Probable ore is ore that is reasonably assured but is not absolutely certain.

Possible ore reflects the prospective value of a mine beyond or below the last visible ore based on the most accurate data from the mine being examined and from the characteristics of the mining district.

Unbroken ore in an ore body is called ore-in-place.

The term ore reserves although commonly quoted in terms of 'proven', 'probable' and 'possible' essentially refers to ore-in-place that has been sufficiently developed by means of drifts, raises and crosscuts to show the necessary grade and tonnage. Broken ore reserves are made up of ore contained in stopes after breaking but will generally include ore contained in other underground workings or in the surface dump.

In a vein type deposit, the wallrock is that rock adjacent to the vein and is usually distinguished as the hanging wall on the upper side and the footwall on the under side. In a general sense the term country rock is comparable to the term wallrock but is generally extended to cover the rock surrounding any orebody (vein or lode type). In a wider sense, it may be applied to the rocks invaded by and surrounding an igneous intrusion.

MINING

A) CONVENTIONAL UNDERGROUND

When a mine is put into operation, a shaft is sunk near the orebody. Horizontal passages are cut from the shaft at various depths to reach the ore. The ore is then removed, (generally), hoisted to the surface, crushed, concentrated and refined. Waste rock or classified mill tailings may be returned to the mine as fill for the mined-out areas or may be directed to a disposal basin (tailings area).

The Shaft

The shaft provides a means of entry or exit for men and materials, and for the removal of ore or waste from underground to surface. It may be vertical or inclined.

NOTE: A passageway or opening driven horizontally into the side of a hill generally for the purpose of exploring or otherwise opening a mineral deposit is called an adit. Strictly speaking, an adit is open to the atmosphere at one end, a tunnel at both ends.

In Ontario, mines have ranged to a depth of 8,250 feet. Although it is unusual for a single shaft to be deeper than 4,000 feet, one shaft has been sunk to a depth of 7,137 feet in the Sudbury area. Shafts may be rectangular (from 5' x 7' to 12' x 30') or circular with a diameter of some 24 feet.

Shafts usually contain from one to eight compartments. Shafts sunk from underground levels are called winzes. Winzes are established to permit mining at depth.

There are generally two types of hoists in use. The 'Koepe' or friction-drive hoist, in common use in Europe since 1875, was first introduced to North America approximately two decades ago. Many are now in service. In this type of hoisting operation, ropes (cables) pass over a drum with counter-balancing weights or loads on either side. These are raised or lowered via friction between the ropes and the drum treads on which they rest. The ropes pass over the drum only once. The arc of contact between rope and drum is normally 180 degrees. On the conventional drum-winder hoist the rope is wound onto the drum and, as such, loads are raised or lowered by a simple winding or unwinding operation.

Shaft conveyances include buckets, skips, cages or skipcage combinations. The first two are for hoisting rock or ore and they vary in load capacity from one to eighteen tons. They travel at approximately 3,000 feet per minute. Cages are used for men and materials and can transport as many as 85 men per load at slower speeds. Safety devices exist to prevent shaft conveyances from falling, should cables fail.

Levels

Levels - horizontal passages in a mine - are generally driven from the shaft at **vertical** intervals of 100 - 200 feet. That part of the level driven from the shaft to the orebody is known as the crosscut, and that part which continues along the orebody is known as a drift. Crosscuts and drifts vary in size from about 2' x 7' to about 9' x 16' depending on the size of the haulage equipment in use.

A raise is an opening made in the back (roof) of a level to reach the level above.

Stopes

A stope is an excavation where the ore is drilled, blasted and removed by gravity through chutes to ore cars on the haulage level below. Stopes require timbered openings (manways) to provide access for men and materials. Normally, raises connect a stope to the level above and are used for ventilation, for convenience in getting men and materials into the stope, and for admitting backfill.

Stoping Methods

The stoping method used normally depends on the stability of the walls and ore as ore removal progresses. There are three common stoping methods used in Ontario:

The Shrinkage Stope:- is used chiefly in narrow regular orebodies where the walls and ore require little support. After each blast, sufficient ore is pulled from the chutes to make room for the miners to drill and blast the next section. As the stope progresses upwards the manways are raised slightly above the level of the broken ore. When the stope reaches the level above, it will be full of broken ore (classed as broken ore reserves). On removal of the ore, the stope may be filled with waste material.

The Cut-and-Fill Stope:- is used in wider irregular orebodies where the walls require support to minimize dilution (waste from the walls falling into the broken ore). A horizontal section of ore about 12 feet high is drilled, blasted and removed. Chutes and manways then are raised to about eight feet from the stope roof. Waste material (or mill tailings) is dumped into the stope through the waste-pass raise until it is level with the chutes and manways. Flooring (wood or concrete) is placed over the fill before the next ore cut is drilled and blasted. Scrapers or diesel endloaders are used to remove ore to the chutes and to level waste backfill in the stope.

The Square-Set Stope:- is used in an orebody where the walls and ore require support during ore removal. After each blast, square-set timbers are erected and made solid by blocking to the walls and back. The chutes and manways are raised and backfill is placed in the stope as in the cut-and-fill method. Flooring - called the mucking floor -

is laid on the backfill at chute elevation. A floor above, supported on the square-sets where drilling and blasting is carried out, is called the mining floor. Square-set timbering protects the miners from loose rock which might fall from the walls and back of the stope.

Safety and Ventilation - The Ontario Mining Act regulates the operation of mines, and requires that a second escapeway be provided for the safety of miners before stoping begins.

Large volumes of fresh air are required to ventilate a mine. This air is delivered from the surface by fans. Some air is drawn off at each level and directed to the working places. Stale air is returned to the surface. Ventilation doors on each level near the shaft station prevent the air from returning to the surface before it has reached the work areas. Special provisions are made for ventilation when diesel equipment is used underground.

B) OPEN PIT OPERATIONS

Whether an orebody will be mined by open-pit or underground methods will be determined by the economics of the operation. In all instances, the total capital and operating costs must be considered. A correct decision is extremely important inasmuch as the equipment for open-pit and underground use is not interchangeable. Further, investment in equipment for either mining method and pre-production stripping expense for open-pit mining must be made long before any returns are received or the method is proven successful. In general, open pit mining is more economical than underground mining especially when the orebody is large and the depth of overburden is not excessive.

Some predominant advantages inherent in the open-pit method are as follows:

a) the open pit method is quite flexible in that it allows for large increases or decreases in production on short notice without rapid deterioration of the workings

b) the method is safe. Loose material can be seen and removed or avoided. Crews can be readily observed at work by supervisors. The relatively small number of men employed contributes to safety.

c) Selective mining is possible without difficulty. Grade control can be easily accomplished by leaving lean sections temporarily unmined or by mining for waste.

d) The total cost of open pit mining,per ton recovered, is usually only a fraction of the cost of underground mining. Further, the cost spread between the two methods is growing wider as larger-scale methods are applied to open pit.

STRIPPING

Material overlying an orebody may consist of earth, sand, gravel, silt, rock or even water. Removal of this material generally falls under the heading of stripping. Normally, stripping of rock will be considered as a "mining" operation. Generally stripping will be accomplished with heavy earth-moving equipment such as the caterpillar type tractor. Suction and cutter dredges are sometimes used. Removal of overburden generally takes place concurrently with construction of the surface plant, after a decision to mine by open pit has been reached.

BREAKING

Drilling

Drilling is the basic part of the breaking operation in open pit mining; considerable effort has therefore been expended to develop equipment for drilling holes at the lowest possible cost. There are several types of drills which can be used. These include churn drills, percussion drills, rotary drills and jet-piercing drills. All are designed with one objective in mind: to produce a hole of require diameter, depth and direction in rock for later insertion of explosives.

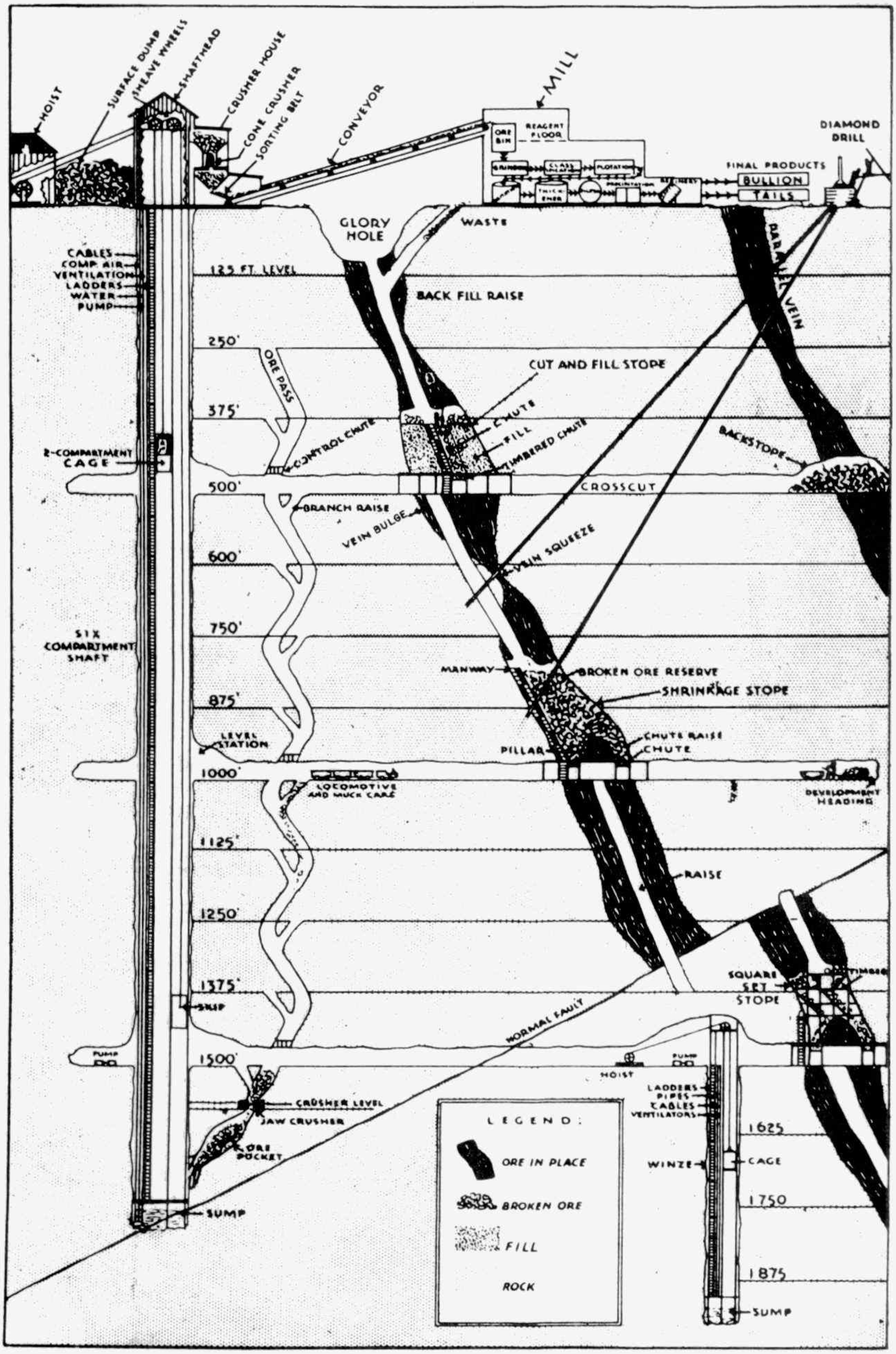
Blasting

Basically, explosives are comprised of chemicals which, when combined, contain all the requirements for complete combustion without external oxygen supply. Early explosives consisted chiefly of nitro-glycerine, carbonaceous material and an oxidizing agent. These mixtures were packaged into cartridges for convenience in handling and loading into holes. Many explosives are still manufactured and packaged to the basic formulas.

In recent years it has been discovered that fertilizer-grade ammonium nitrate mixed with about 6 percent fuel oil could be detonated by a high explosive primer. This new application has spread to the point where virtually all open pit mining companies use this mixture for some or all of the primary blasting. Secondary blasting is usually done at the end of a shift by means of cartridge explosives and electric caps. However, as pit equipment becomes larger and as the scale of operations increases, secondary blasting becomes a relatively smaller part of the mining operation.

LOADING

After the ore has been broken, it is transferred to the mill for treatment. Although a variety of loading equipment is used in open pit mines depending on the scale of operations, the power shovel seems to be preferred.



SKETCH OF IDEALIZED SECTION THROUGH THE WORKINGS OF A TYPICAL SMALL MINE. LEVEL DETAILS ARE GIVEN AT ONLY EVERY FOURTH HORIZON.

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"Mining Explained" by Northern Miner Press Limited, Publications Division, 77 River Street, Toronto 247, Ontario, Canada.

"Open Pit Mining Practice in Canada" by A. Dubnie, Mineral Resources Division, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada.

A GENERAL LOOK AT SULPHIDE MILLING

Each sulphide operation attempts to remove locally as much of the waste rock as possible from its ore and ship the enriched product to a strategically located smelter. This process of removing the waste rock and separating the valuable sulphides of the metals is termed concentrating. The mill is a concentrator and the product is a concentrate.

Ores generally consist of a complex mixture of valuable and non-valuable particles. The valueless particles are referred to as "gangue".

In a complex sulphide ore it is possible to have microscopic particles of one sulphide species existing as cores within small blebs of other sulphide species (for example, sphalerite within galena). The purpose of crushing and grinding the ore in the mill, therefore, is to cleanly liberate all the desirable constituents of the ore so that each may be recovered as a separate concentrate.

It is unusual in most ores to effect good liberation of values at sizes coarser than 200 mesh. However, if the crushing and grinding part of the process is not controlled very carefully, a fraction of sub-micron sizes are produced and these may interfere with subsequent operations. Thus, in sulphide milling, the objective is to reduce the ore in size to a degree of fineness which gives an economic liberation of the valuable mineral or minerals but which avoids as much as possible the production of sliming fractions.

Crushing

After the ore is broken underground in the mine, it is generally sent to the surface for storage in a coarse ore bin. When required, the coarse ore bin feeds a primary crusher. This is usually a jaw crusher which consists essentially of a fixed vertical jaw or plate, and a movable jaw at a slight vertical angle; the movable jaw being pushed backwards and forwards by a system of toggles. The rock falls into the opening between the jaws at the top of the crusher and is crushed by the rapid, but short, forward motion of the movable jaw. The plates converge towards the bottom and thus the rock may be pinched and shattered several times before it falls free of the bottom opening.

NOTE: In some cases, the primary crusher may be installed underground at the bottom of the ore pass system. This facilitates skip loading since unwieldly pieces of ore are eliminated.

The size of a jaw crusher is designated by the horizontal dimensions of the top openings. For example, a 15 inch by 24 inch crusher has an opening 15 inches wide and 24 inches long. It will take pieces of rock 12 inches thick and reduce them to a minimum of 2 inches at a rate of 25 tons per hour. A 40 hp motor will drive the crusher.

Customary crusher sizes range from 9 inches by 15 inches (for a 50 ton per day mill) to larger than 60 inches by 84 inches.

The jaw crusher is not an efficient machine (few milling machines are). It is built of either steel plate or cast steel since it must be able to withstand intense shocks. A heavy pair of flywheels are included to smooth power requirements.

A few large tonnage concentrators use a gyratory crusher for the primary breaker. It consists of a heavy gyratory crushing head mounted on a vertical shaft. The head works inside a crushing bowl that is fixed to the main frame. Rock introduced into the bowl is caught and nipped by the gyrating head. It then falls through an opening of predetermined size. Gyratory crushers, usually installed on the surface at large mining properties, can handle three or four hundred tons per hour.

The need for a secondary crusher frequently arises when the product from the primary crusher is too large for efficient grinding. In Canada, the main type used is the Symons cone crusher which may be considered a cousin of the gyratory. However, its speed is greater and it is designed to take a feed of 4 to 6 inches and reduce it to one inch or finer.

Crushing is done dry and usually takes place in a building separate from the mill or concentrator. Capacity is usually such that the entire daily tonnage requirement is crushed in one or two shifts. This permits balancing of power loads and labour requirements and provides opportunity for repairs.

Size control of the crusher house product is generally achieved with the use of a vibrating screen. The oversize from the screen is returned for further crushing. The remainder of the material is directed to fine ore storage bins (which feed the grinding circuit).

Crusher houses are generally equipped with dust control and ventilation systems which are designed to eliminate any build-up of dust particles in the air.

It is necessary to provide mill-feed storage on the surface at a mining operation since a mill (or concentrator) usually operates 24 hours per day -- seven days per week whereas a mine and crusher plant may only work six days per week. At least thirty hours' requirements of crushed ore are generally available in the fine ore storage bins.

Grinding

Ore from the fine ore bins, along with water, is directed to one or more grinding units in the mill. Each unit generally consists of a ball or rod mill that operates with or without a classifier.

A ball mill consists of a horizontal cylindrical revolving shell that is supported on hollow trunnion bearings. The ore enters through one trunnion opening and is discharged through the other. The mill is kept about half full of steel balls which, as the mill revolves, cascade and roll over each other. It is this action that crushes the ore. As the balls wear smaller they form a charge of graduated size and therefore, only balls of the largest size are added to maintain the ball charge. The size of the new balls in any particular mill varies from three-quarters of an inch to approximately five inches. The size is dependent on the size of the mill feed and on the toughness of the ore itself.

A rod mill differs from a ball mill in that steel rods instead of steel balls are used as the grinding media. The rods are from 2 to 4 inches in diameter and are approximately the length of the interior of the mill itself.

Autogenous grinding units are becoming quite common. These units force the ore to crush and grind itself. Rods and balls are eliminated. Autogenous mills can be either wet or dry.

Classification

The usual function of a classifier in a sulphide mill circuit is to perform a physical separation that results in oversize particles being returned to mills for further grinding.

In operation, the pulp discharged from a grinding mill flows down a launder to a classifier. The classifier generally takes the form of a long inclined tank that has been equipped with a rake-type mechanism that is able to move sandy material up the incline. The pulp from a mill enters the bottom end of the inclined tank where the heavier, coarser particles settle and are caught and moved up the incline by the rake mechanism to the top end of the tank. From here, the coarse particles flow by gravity into the feed end of a grinding mill. The fine particles that do not settle at the bottom end of the tank are carried, as finished particles, by a current of controlled velocity over an adjustable weir and are directed to the next stage of the process (usually flotation).

Many kinds of classifiers especially those which operate on a centrifugal principle, are coming into wide use in newer plants.

Grinding in closed circuit is a term used to describe a (ball) mill and a classifier that work together as a unit. The material so produced will have a certain maximum size. The finest size produced is controlled to some extent.

A rod mill may be used to prepare feed for a ball mill. In this case, it may function without a classifier and this is termed open circuit operation.

Flotation

Flotation, or more specifically froth flotation, is a physico-chemical method of concentrating finely ground sulphide ores. The process involves chemical treatment of an ore pulp to create conditions favourable for the attachment of certain mineral particles to air bubbles. The air bubbles carry the selected minerals to the surface of the pulp and form a stabilized froth which is skimmed off while the other minerals remain submerged in the pulp.

In general, sulphide mineral particles coarser than 48 mesh (about 295 microns or 0.295 mm in diameter) cannot be effectively recovered; consequently, an ore that is to be floated must first be ground fine enough so that the desired mineral particles are all, or substantially all, smaller than this limiting size.

The creation of a rising current of air bubbles is accomplished by a flotation machine which produces bubbles by mechanical agitation of the ore pulp, the direct introduction of air under pressure, or both. These operations may be considered as the mechanical adjuncts of the flotation process.

To obtain the adherence of the desired mineral particles to the air bubbles and hence the formation of a mineral-laden froth on the surface of the ore pulp, a hydrophobic surface film must be formed on the particles to be floated and a hydrophilic or wettable film on all others. This is done by adding various chemicals. The selection of these chemicals for each particular ore constitutes the principal problem of the ore dressing metallurgist.

All flotation concentration processes are selective or differential in that one mineral or group of minerals is floated away from accompanying gangue. Ordinarily, however, the separation of unlike minerals, such as sulphides from nonsulphides, is referred to as "bulk flotation" and the term "differential flotation" is restricted to operations involving separations of similar mineral types. Differential flotation may be exemplified by the concentration and subsequent successive removal of copper, lead, zinc and iron sulphides from a single ore.

Thickening

It is sometimes necessary to increase the solids content of an ore pulp. The machine that does this is called a thickener. Operating continuously, a thickener is a large diameter, comparatively shallow, round tank. As the feed enters, the entrained rock particles sink to the bottom of the thickener and are raked to a discharge mechanism located in the centre of the tank floor. Some of the extremely fine particles in the feed are aided in settling by the addition of chemicals such as lime. The underflow from a thickener tends to resemble a sludge; the resultant clear solution in the thickener overflows the top of the tank and is collected in a launder.

Filtration

Some form of filtration is required in most mine-mill circuits. In many cases, a filter will take the form of a large, horizontally-mounted, revolving drum. The drum is porous and partially submerged in a semi-circular steel tank which receives pulp from specific mill processes. As the drum rotates, a vacuum is applied from within which causes a definite thickness of pulp to adhere to the drum. The resultant "cake" is scraped off continuously. The final concentrate from a sulphide mine-mill operation is generally formed in this way.

References used in this section:

"Mining Explained" by Northern Miner Press Limited, Publications Division, 77 River Street, Toronto 247, Ontario, Canada.

THE SULPHIDES AND SULPHOSALTS

In most sulphide milling circuits, the iron sulphides pyrite, marcasite and pyrrhotite are rejected and sent to the tailings area as waste. The iron sulphides (indeed all sulphide species) are seldom pure, often occur as intimate mixes and frequently contain inclusions of other "ore" sulphides and/or sulphosalts. As the iron sulphides decompose, the associated "ore" sulphides and sulphosalts are exposed to extreme chemical conditions and, as such, tend to break down themselves. This breakdown results in the release of diverse metallic and non-metallic ions to the immediate environment. More important, however, is the fact that present day milling technology rarely permits 100 percent recovery of any ore material. To be more specific, a sulphide mining operation rarely enjoys a mill efficiency of greater than 97 percent and, as such, limited quantities of "ore" sulphides continually gain access to a particular tailings area while the mill is operating. These ore materials therefore become an integral part of the tailings mass and enter into oxidation reactions that, in a simple sense, tend to resemble the oxidation reactions of the iron sulphides. Again, diverse metallic and non-metallic ions gain access to the local environment.

When the correct conditions are presented, sulphide (and sulphosalt) minerals in a tailings mass will oxidize to the corresponding metal ions plus the sulphate ion. Generally speaking, the sulphate ion will leave the tailings area. The metal ions on the other hand, depending on many chemical factors, may be precipitated as "insoluble" hydroxides, oxides, carbonates, sulphates, or silicates, etc., and hence be retained within the tailings area or may be carried away in solution from the site of oxidation and hence leave the tailings area. Iron, copper, cobalt, manganese, zinc and nickel all form soluble salts (usually sulphates) under acid mine drainage conditions and are therefore commonly detected in the effluents from affected areas. Lead, on the other hand, forms a relatively insoluble sulphate (known as the mineral anglesite in geology texts) and is therefore only rarely detected in concentrations greater than 1 part per million under similar circumstances.

It is perhaps necessary to explain just what we mean when we use the term"sulphide" and the term "sulphosalt". Sulphides and sulphosalts are analogous to simple oxides and multiple oxides.

The general formula for a sulphide is A_mX_n where

A consists of the metallic elements principally, and less frequently arsenic, antimony and bismuth as the table below shows:

Elements In the Sulphides

		A			X	
Ag	Fe	Pb	As	Ru*	S	As
Cu	Co	Hg	Sb*	Sn*	Se	Sb*
Tl*	Ni	Mn*	Bi*	Mo*	Te	Bi*
Au*	Zn	Ca*	Pt*	W*		
		Cd				

*Rare or uncommon

The sulphosalts (general formula $A_mB_nX_p$) have very few elements as major constituents:

A	B	X
Cu	As	S
Ag	Sb	
Pb	Bi	
Sn	Sn	

However, when the number of species and the complexities of composition are considered, this class of minerals shows almost as much diversity in combinations of the same chemical elements as do the silicates.

The fact that a sulphide ore body contains many more sulphide species than the few main species being recovered is of extreme importance. Many metals will appear in the effluents from a sulphide mining operation and the actual metals (that will appear) cannot be determined solely on the basis of the main sulphide species known to be present. For instance, assume a property works an ore body containing the three ore sulphides chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS). We know that lead forms a relatively insoluble sulphate and therefore we would not expect a significant concentration of lead in the effluents should an acid mine drainage situation arise. We would expect significant concentrations of copper, iron and zinc. However, it is known that chalcopyrite occasionally contains among others gold, silver, selenium and thallium; galena is associated with materials such as silver, antimony, arsenic, selenium, iron, zinc, cadmium, copper, gold and platinum; and sphalerite with iron, manganese, cadmium, mercury, indium, gallium, thallium, gold and silver. In other words, the complete dissolution of the chalcopyrite or the galena or the sphalerite will release at least trace quantities of metals that at first glance would not be expected in the effluents from that particular property.

The following is a list of 125 naturally occurring sulphides and sulphosalts. A few other species are known but are vaguely described. In the list, each sulphide or sulphosalt is treated separately. The chemical formula for each is given as accurately as possible as are typical analyses based on samples of each. Trace elements have been included for some species.

Note: The first column of analytical results for each mineral listed represents, for convenience, the empirical analysis of the sulphide or sulphosalt. The list is presented on the basis of a chemical-structural order rather than alphabetical order. However, the list in the index of this report is presented in alphabetical order.

"Typical Analyses" quoted in this section were adapted from "DANA'S SYSTEM OF MINERALOGY" by Palache, Berman and Frondel, SEVENTH EDITION, VOLUME 1, John Wiley & Sons.

SULPHIDES AND SULPHOSALTS

(1) Name: Tetradymite

Formula: Bi_2Te_2S

Typical Analyses:

Bi	59.27	62.23	60.53	60.36	59.66	59.56	59.12	56.35
Te	36.19	33.25	33.34	35.25	36.16	35.46	35.94	35.62
S	4.54	4.50	4.23	4.20	4.54	4.98	4.75	4.38
Se	--	--	1.46	trace	--	trace	--	2.17
Rem.	--	--	0.68	--	0.82	--	--	1.48
Total:	100.00	99.98	100.24	99.81	98.18	100.00	99.81	100.00

Alteration Products:

usually montanite $Bi_2O_3.TeO_3.2H_2O$

also bismutite $Bi_2O_3.CO_2.H_2O$

observed coated by native gold

(2) Name: Gruenlingite

Formula: Bi_4TeS_3 or near $Bi_2(Te, Bi)S_2$

Typical Analyses:

Bi	78.89	79.07
Te	12.03	12.74
S	9.08	9.37
Total:	100.00	101.18

(3) Name: Joseite

Formula: perhaps $Bi_3Te(Se, S)$

Typical Analyses:

Bi	79.71	79.15	78.40	81.23
Te	16.21	15.93	15.68	14.67
Se	--	1.48)	4.58	2.84
S	4.08	3.15)		1.46
Total:	100.00	99.71	98.66	100.20

Alteration Products:

montanite (?) $Bi_2O_3.TeO_3.2H_2O$

(4) Name: Wehrlite

Formula: Uncertain, perhaps Bi_8Te_5S

Typical Analyses:

Ag	2.07	0.48	4.37
Bi	61.15	70.02	59.47
Te	29.74	28.52	35.47
S	2.33	1.33	--
Total:	95.29	100.35	99.31

(5) Name: Nagyagite

Formula: Uncertain, $Pb_5Au(Te, Sb)_4 S_{5-8}$

Typical Analyses:

Pb	57.16	56.81	55.44	54.50	53.55	52.55	51.18
Au	7.41	7.51	8.43	7.61	9.47	10.16	8.11
Sb	6.99	7.39	6.61	8.62	6.05	7.00	--
Te	17.87	17.72	18.92	17.80	18.99	18.80	29.88
S	10.01	10.76	9.69	9.10	11.90	8.62	10.83
Rem.	0.60	0.41	0.90	3.05	0.56	1.12	--
Total:	100.04	100.60	99.99	100.68	100.52	98.25	100.00

Alteration Products:

Pseudomorphs after nagyagite of chalcopyrite ($CuFeS_2$), bournonite ($2PbS.Cu_2S.Sb_2S_3$), and of galena (PbS) mixed with gold have been described.

(6) Name: Argentite

Formula: Ag_2S

Typical Analyses:

Ag	87.06	86.71	71.65
Cu	--	--	13.97
S	12.94	13.13	16.17
Total:	100.00	99.84	101.79

Alteration Products:

alters to native silver, silver sulphosalts and other silver minerals.

(7) Name: Aguilarite

Formula: Ag_4SeS

Typical Analyses:

Ag	79.50	79.07	79.41	80.27	84.40
Cu	--	--	0.50	0.07	0.49
Fe	--	--	--	0.26	--
S	5.91	5.86	5.93	6.75	11.36
Se	14.59	14.82	13.96	12.73	3.75
Sb	--	--	--	0.41	--
Total:	100.00	99.75	99.80	100.49	100.00

Alteration Products:

native silver (?)

cuprian stephanite 5 $Ag_2S.Sb_2S_3$

(8) Name: Digenite

Formula: $Cu_{2-x}S$

Typical Analyses:

Cu	78.85	78.96	78.11	77.99	76.59	76.19	75.30
Fe	--	--	none	0.26	0.20	0.37	0.16
S	21.15	20.62	21.85	21.48	23.21	23.44	24.54
Rem.	--	0.42	--	0.13	--	--	--
Total:	100.00	100.00	99.96	99.86	100.00	100.00	100.00

Alteration Products:

native copper (Cu), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covellite (CuS), malachite $CuCO_3.Cu(OH)_2$, azurite $2CuCO_3.Cu(OH)_2$

(9) Name: Chalcocite

Formula: Cu_2S

Typical Analyses:

Cu	79.86	79.67	79.30	79.65	79.50
Fe	--	0.14	0.18	--	0.17
S	20.14	20.16	20.04	20.02	20.05
SiO_2	--	0.09	--	0.06	0.17
Gangue	--	--	0.30	--	--
Rem.	--	--	0.18	0.20	--
Total:	100.00	100.06	100.00	99.93	99.89

(10) Name: Stromeyerite

Formula: $AgCuS$

Typical Analyses:

Ag	53.01	53.31	52.10	51.80	48.64
Cu	31.24	31.00	32.14	31.46	30.64
Fe	--	trace	--	0.30	0.20
Zn	--	--	--	--	3.28
Pb	--	--	--	--	1.53
S	15.75	16.02	15.26	16.08	16.23
Insol.	--	--	--	0.32	--
Total:	100.00	100.33	99.50	99.96	100.52

(11) Name: Bornite

Formula: Cu_5FeS_4

Typical Analyses:

Cu	63.33	63.90	63.24	63.08	62.99	63.20	63.24
Fe	11.12	10.79	11.12	11.22	11.23	11.34	11.20
Pb	--	none	--	none	0.10	--	--
Ag	--	none	--	none	none	--	--
S	25.55	25.17	25.54	25.54	25.58	25.65	25.54
Total:	100.00	99.86	99.90	99.84	99.90	100.19	99.98

Alteration Products:

chalcocite Cu_2S
chalcopyrite $CuFeS_2$
covellite CuS
cuprite Cu_2O
chrysocolla $CuSiO_3.2H_2O$
malachite $CuCO_3.Cu(OH)_2$
azurite $2\ CuCO_3.Cu(OH)_2$

(12) Name: Dimorphite

Formula: As_4S_3

Typical Analyses:

As	75.70	75.45
S	24.30	24.55
Total:	100.00	100.00

(13) Galena

Formula: PbS

Typical Analyses:

Pb 86.60, S 13.40, Total 100.00

The silver given in most galena analyses is presumably due to admixed silver minerals such as argentite (Ag_2S) and tetrahedrite ($3Cu_2S.Sb_2S_3+Ag$). As and Sb are due to impurities. The elements Se, Fe, Zn, Cd, Cu and sometimes Au, Pt have been reported but without proof that the analyzed material was homogeneous.

Alteration Products:

cerussite ($PbCO_3$), anglesite ($PbSO_4$), pyromorphite ((Pb_4 (Pb, Cl)$(PO_4)_3$), mimetite (Pb_4 (Pb, Cl)$(AsO_4)_3$), phosgenite $PbCO_3.PbCl_2$ and cotunnite $PbCl_2$.

(14) Name: Alabandite

Formula: MnS

Typical Analyses:

Mn	63.14	63.03
S	36.86	36.91
Total:	100.00	99.94

(15) Name: Oldhamite

Formula: CaS

Known only to occur in meteorites.

(16) Name: Sphalerite

Formula: ZnS

Typical Analyses:

Sn	--	1.4	--	--	0.45	--	--	--
Fe	--	26.2	2.33	7.99	0.40	18.25	0.15	11.05
Mn	--	--	--	trace	--	2.66	--	--
Cd	--	--	0.95	1.23	--	0.28	--	0.30
Zn	67.10	37.6	63.36	57.38	65.44	44.67	66.98	55.89
S	32.90	34.7	32.94	32.99	33.38	33.57	32.78	32.63
Gangue	--	--	0.40	--	--	--	--	--
Total:	100.00	99.9	99.98	99.59	99.67	99.43	99.91	99.87

Alteration Products:

goslarite $ZnSO_4.7H_2O$

hemimorphite H_2ZnSiO_5 or $H_2O.2ZnO.SiO_2$

smithsonite $ZnCO_3$

(17) Name: Metacinnabar

Cinnabar

Formula: HgS

Typical Analyses:

Hg	86.22	77.68	79.73	79.69	83.38	81.33
Fe	--	5.36	trace	1.04	--	--
Zn	--	--	4.23	3.32	2.17	--
Se	--	--	1.08	--	--	6.49
S	13.78	14.97	14.58	14.97	14.24	10.30
Rem.	--	1.41	--	--	0.52	--
Total:	100.00	99.42	99.62	99.02	100.31	98.12

Alteration Products:

Metacinnabar reverts to the stable form of HgS called cinnabar.

(18) Name: Chalcopyrite

Formula: $CuFeS_2$

Typical Analyses:

Cu	34.64	33.60	33.10	31.5	33.54	34.36
Fe	30.42	30.92	30.60	32.4	31.78	30.61
S	34.94	34.90	35.12	36.5	33.97	35.01
SiO_2	--	--	1.43	--	0.90	--
Total:	100.00	99.42	100.25	100.4	100.19	99.98

Alteration Products:

- changes to sulphate on exposure with moisture
- alters to chalcocite Cu_2S, covellite CuS, chrysocolla $CuSiO_3.2H_2O$, malachite $CuCO_3.Cu(OH)_2$, melaconite (essentially CuO), and iron oxides.

(19) Name: Stannite

Formula: Cu_2FeSnS_4

Typical Analyses:

Cu	29.58	31.52	29.00	29.38	29.24
Fe	12.99	12.06	13.75	13.89	13.95
Sn	27.61	27.83	27.50	27.20	27.14
Zn	--	--	0.75	0.02	0.08
S	29.82	28.59	29.00	28.77	28.88
Insol.	--	--	--	0.62	0.51
Total:	100.00	100.00	100.00	99.88	99.80

(20) Name: Wurtzite

Formula: ZnS (see sphalerite #16)

Typical Analyses:

Fe	--	2.43	6.02
Zn	67.10	62.64	59.70
Cd	--	1.84	1.07
Pb	--	0.41	0.15
S	32.90	32.10	32.90
Gangue	--	0.30	0.13
Total:	100.00	99.72	99.97

Alteration Products:

Wurtzite inverts to sphalerite (ZnS)

(21) Name: Greenockite

Formula: CdS

Typical Analyses:

Cd 77.81, S 22.19, Total 100.00

The few analyses available differ only slightly from the theoretical composition.

Greenockite is usually found as an earthy coating on zinc minerals, especially sphalerite.

(22) Name: Voltzite

Formula: Zn_5S_4O

Typical Analyses:

- an oxysulphide of zinc: Zn 69.38, S 27.22, O 3.40, Total 100.00

- modern analyses are lacking

(23) Name: Pyrrhotite

Formula: $Fe_{1-x}S$ (x lies between 0 and 0.2)

Typical Analyses:

Ni, although reported in most analyses has been shown to be due, for the most part, to admixed pentlandite $(Fe, Ni)_9S_8$. Small amounts of Co, Mn, Cu, generally less than 1 percent, are often reported.

Cu	--	0.06	1.1	--	--	--	--	--
Fe	63.53	61.49	60.4	59.62	59.91	60.18	61.29	60.87
Co	--	--	--	--	0.12	--	--	--
Ni	--	0.39	0.3	--	0.61	--	--	--
S	36.47	37.18	38.1	39.33	39.69	39.82	37.97	36.56
Insol.	--	0.46	--	0.61	--	--	--	--
SiO_2	--	--	--	--	--	--	0.82	2.42
Total:	100.00	99.58	99.9	99.56	100.33	100.	100.08	99.85

Alteration Products:

Alters by oxidation to iron sulphates, limonite ($Fe_2O_3.nH_2O$) and siderite $FeCO_3$.

(24) Name: Millerite

Formula: NiS

Typical Analyses:

Ni 64.67, S 35.33, Total 100.00. Old analyses give small amounts of Co, Fe and Cu.

(25) Name: Pentlandite

Formula: $(Fe, Ni)_9S_8$

Typical Analyses:

Fe	32.55	30.68	30.25	30.04	30.00
Ni	34.22	34.48	34.23	34.98	34.82
Co	--	1.28	0.85	0.85	0.84
S	33.23	32.74	33.42	33.30	32.90
Insol.	--	0.56	0.67	0.83	1.44
Total:	100.00	99.74	99.42	100.00	100.00

(26) Name: Cubanite

Formula: $CuFe_2S_3$

Typical Analyses:

Cu	23.42	24.32	23.57	23.52	22.96	22.88	22.27
Fe	41.15	41.15	41.24	41.14	42.51	41.41	43.13
S	35.43	34.37	36.00	35.30	34.78	35.35	35.11
Total:	100.00	99.84	100.81	99.96	100.25	99.64	100.51

(27) Name: Sternbergite

Formula: $AgFe_2S_3$

Typical Analyses:

Ag	34.17	35.27	33.2	30.69	29.1
Fe	35.37	35.97	36.0	35.44	37.4
S	30.46	29.10	30.0	33.87	33.0
Total:	100.00	100.34	99.2	100.00	99.5

(28) Name: Covellite

Formula: CuS

Typical Analyses:

Cu	66.48	66.06	66.43	65.49
Fe	--	0.14	0.05	0.25
S	33.52	33.87	33.28	33.45
Insol.	--	0.11	0.07	--
Total:	100.00	100:18	99.83	99.19

Alteration Products:

Covellite is derived from the alteration of a number of copper minerals, notably chalcopyrite $CuFeS_2$, chalcocite Cu_2S, bornite Cu_5FeS_4, and stromeyerite AgCuS.

(29) Name: Realgar

Formula: AsS

Typical Analyses:

As	70.0	69.57	69.54	69.74
S	30.0	30.55	30.24	29.82
Rem.	--	--	0.11	0.15
Total:	100.00	100.12	99.94	99.71

Alteration Products:

On exposure to light changes to orpiment As_2S_3, and arsenolite As_2O_3.

(30) Name: Cooperite

Formula: PtS

Typical Analyses:

Pt	85.89	85.6	82.5	80.26	82.2
Pd	--	trace	--	4.31	2.6
Ru, Ir etc.	--	--	--	0.62	--
Ni	--	0.1	--	trace	--
S	14.11	14.3	17.5	14.36	14.4
Total:	100.00	100.0	100.0	99.55	99.2

(31) Name: Braggite

Formula: (Pt, Pd, Ni)S

Typical Analyses:

Pt	60.15	58.2	59.1
Pd	18.27	18.1	20.87
Ni	4.02	4.7	2.8
S	17.56	19.0	16.8
Total:	100.00	100.0	99.6

(32) Name: Linnaeite Series

Formula: $(Co, Ni)_2\ (Co, Ni, Fe, Cu)S_4$

i.e., Linnaeite Co_3S_4
Siegenite $(Co, Ni)_3S_4$
Carrollite Co_2CuS_4
Violarite Ni_2FeS_4
Polydymite Ni_3S_4

Typical Analyses:

Cu	2.40	8.79	--	3.16	20.42	18.98	1.12	--
Fe	2.36	1.30	0.62	3.22	2.33	0.93	17.01	3.98
Co	48.70	40.71	26.08	20.36	35.30	35.79	1.05	0.63
Ni	4.75	7.35	31.18	31.24	1.76	3.66	38.68	54.30
S	41.70	41.43	42.63	42.43	39.47	40.64	41.68	41.09
Insol.	0.40	0.14	0.16	--	--	--	0.40	--
Total:	100.31	99.72	100.67	100.41	99.28	100.00	99.94	100.00

Alteration Products:

Alters to a mixture of erythrite $Co_3As_2O_8.8H_2O$ and pitticite $Fe_2(AsO_4)(SO_4)(OH).nH_2O$.

(33) Name: Daubreelite

Formula: Cr_2FeS_4

Typical Analyses:

Cr	36.10	35.91
Fe	19.38	20.10
S	44.52	42.69
Total:	100.00	98.70

(34) Name: Orpiment

Formula: As_2S_3

Typical Analyses:

As 60.91, S 39.09, Total 100.00

The few available analyses are close to the stated formula.

Alteration Products:

Often observed as an alteration product of realgar AsS, native arsenic As, and less commonly arsenopyrite FeAsS.

(35) Name: Stibnite

Formula: Sb_2S_3

Typical Analyses:

Pb	--	--	--	--	0.23
Cu	--	--	--	--	0.09
Fe	--	--	--	0.11	0.12
Sb	71.69	71.45	71.51	71.84	71.83
S	28.31	28.42	28.66	28.25	26.90
Total:	100.00	99.87	100.17	100.20	99.17

Alteration Products:

To kermesite Sb_2S_2O and, on complete oxidation to cervantite $Sb_2O_3.Sb_2O_5$, stibiconite $H_2Sb_2O_5$, senarmontite Sb_2O_3, valentinite Sb_2O_3.

(36) Name: Bismuthinite

Formula: Bi_2S_3

Typical Analyses:

Pb	--	0.69	1.68	--	1.51	--	--
Cu	--	0.57	0.48	0.57	0.57	--	--
Fe	--	0.40	0.74	0.17	0.66	--	--
Bi	81.3	80.04	79.28	79.47	79.04	76.51	76.94
Sb	--	--	--	--	--	3.58	--
Te	--	--	--	0.94	--	--	--
Se	--	--	--	--	--	--	8.80
S	18.7	18.46	18.46	18.42	18.40	20.07	14.15
Insol.	--	--	--	0.50	0.35	--	--
Total:	100.0	100.16	100.64	100.07	100.53	100.16	99.89

Alteration Products:

Alters readily to various ill-defined bismuth carbonates and to bismite (?) Bi_2O_3.

(37) Name: Kermesite

Formula: Sb_2S_2O

Typical Analyses:

Sb	75.24	75.13
S	19.82	20.04
O	4.94	4.83
Total:	100.00	100.00

(38) Name: Pyrite

Formula: FeS_2

Typical Analyses:

Fe	46.55	46.49	46.49	--	--	29.30	45.20	33.32
Ni	--	--	--	--	--	16.69	--	0.19
Co	--	--	--	--	--	trace	1.25	13.90
S	53.45	53.49	--	53.53	53.46	53.40	53.30	52.45
SiO_2	--	0.04	--	--	--	--	0.30	--
Total:	100.00	100.02	--	--	--	99.39	99.78	99.86

Alteration Products:

Pyrite changes readily by oxidation to various iron sulphates, or, as an end product of the process, to limonite $Fe_2O_3.nH_2O$. The sulphuric acid generated in the oxidation of pyrite plays an important role in the formation of zones of enrichment in ore deposits, especially of copper, and as such has received careful study in the field and in the laboratory.

(39) Name: Bravoite

Formula: $(Ni, Fe)S_2$

Typical Analyses:

Fe	23.00	17.08	21.15	20.68
Ni	24.17	24.73	17.50	24.81
Co	--	3.28	6.61	--
Cu	--	0.47	--	--
S	52.83	51.15	53.70	54.51
Rem.	--	0.40	1.04	--
Total:	100.00	97.11	100.00	100.00

(40) Name: Laurite

Formula: RuS_2

Typical Analyses:

Ru	61.1	65.18	67
Os	--	3.03	--
S	38.9	31.79	33
Total:	100.0	100.00	100

(41) Name: Hauerite

Formula: MnS_2

Typical Analyses:

Mn	46.14	46.47	46.28
Fe	--	0.03	--
S	53.86	53.27	53.51
SiO_2	--	0.16	--
Total:	100.00	99.93	99.79

Alteration Products:

The surface of the mineral is usually dull black owing to an alteration coating of uncertain composition.

(42) Name: Cobaltite

Formula: CoAsS

Typical Analyses:

Fe	--	4.11	2.92	4.55
Co	35.53	28.64	32.36	29.10
Ni	--	3.06	0.32	0.97
As	45.15	44.77	42.88	44.55
S	19.32	19.34	21.48	20.37
Total:	100.00	99.92	99.96	99.54

(43) Name: Gersdorffite

Formula: NiAsS

Typical Analyses:

Cu	--	4.20	1.10	1.26	--	--	--	--
Fe	--	5.71	8.89	10.16	3.9	--	8.99	1.98
Co	--	--	1.72	0.40	0.7	--	0.89	--
Ni	35.42	23.48	28.92	31.67	31.6	33.32	32.81	28.86
Sb	--	0.54	1.63	1.61	9.1	1.15	1.89	13.45
As	45.23	44.33	43.54	42.02	34.9	45.50	39.34	37.83
S	19.35	17.76	13.84	12.99	17.1	19.37	15.56	17.19
Rem.	--	3.98	--	--	0.4	0.66	--	--
Total:	100.00	100.00	99.64	100.11	97.7	100.00	99.48	99.31

(44) Name: Ullmannite

Formula: NiSbS

Typical Analyses:

Fe	--	0.03	0.17	trace	0.40	0.28
Ni	27.62	27.82	28.17	13.41	28.91	26.94
Co	--	0.65	trace	13.88	1.13	0.89
Sb	57.30	57.43	55.73	56.78	42.93	44.94
As	--	--	0.75	--	10.28	2.02
Bi	--	--	--	--	0.68	11.76
S	15.08	14.02	14.64	15.78	16.22	14.39
Rem.	--	--	0.11	--	--	--
Total:	100.00	99.95	99.57	99.85	100.55	101.22

Alteration Products:

An alteration product gave the composition Sb 52.44, O 16.15, CaO 13.52, NiO 3.27, FeO 3.13, MgO 0.21, H_2O 11.26, Total 99.98

(45) Name: Loellingite

Formula: $FeAs_2$

Typical Analyses:

Fe	27.15	22.96	23.75	21.22	31.20	28.70
Co	--	4.37	4.13	6.44	--	--
Ni	--	0.21	0.20	--	--	--
Bi	--	0.08	--	--	--	--
Sb	--	--	0.29	5.61	--	--
As	72.85	71.18	70.16	63.66	61.40	71.09
S	--	0.56	1.20	3.66	6.73	trace
Rem.	--	0.39	--	--	--	--
Total:	100.00	99.75	99.73	100.59	99.33	99.79

Alteration Products:

To scorodite $FeAsO_4.2H_2O$, pharmacosiderite $6FeAsO_4.2Fe(OH)_3.12H_2O$, symplesite $Fe_3As_2O_8.8H_2O$.

(46) Name: Marcasite

Formula: FeS_2

Typical Analyses:

Fe	46.55	46.53	46.55	47.22	46.56
S	53.45	53.30	53.05	52.61	53.40
Rem.	--	0.20	--	--	0.05
Total:	100.00	100.03	99.60	99.83	100.01

Alteration Products:

$FeSO_4.7H_2O$, H_2SO_4, $Fe_2O_3.nH_2O$

(47) Name: Arsenopyrite

Formula: FeAsS

Typical Analyses:

Fe	34.30	34.53	34.61	30.21	34.92	29.65	31.42	35.23
Co	--	0.09	--	0.76	0.29	3.05	3.07	--
Ni	--	--	--	--	0.73	--	--	--
Bi	--	0.79	--	4.13	--	--	--	--
Sb	--	--	--	1.90	--	--	--	--
As	46.01	44.34	40.82	39.96	41.50	47.60	45.77	41.77
S	19.69	20.22	22.65	15.92	19.12	19.70	19.74	22.59
Rem.	--	--	1.92	7.12	2.81	--	--	0.55
Total:	100.00	99.97	100.00	100.00	99.37	100.00	100.00	100.14

Alteration Products:

Scorodite $FeAsO_4.2H_2O$, pitticite $Fe_2(AsO_4)(SO_4)(OH).nH_2O$, pharmacosiderite $6FeAsO_4.2Fe(OH)_3.12H_2O$, rarely realgar AsS. The cobaltian varieties alter to erythrite $Co_3As_2O_8.8H_2O$.

(48) Name: Glaucodot

Formula: (Co, Fe) AsS

Typical Analyses:

Fe	22.72	21.39	19.60	13.68	5.33	16.27
Co	11.99	17.37	16.68	22.24	31.64	18.64
Ni	--	0.46	trace	--	--	--
Bi	--	--	--	--	0.10	--
As	45.72	41.22	44.01	43.79	42.97	45.84
S	19.57	19.56	20.18	20.29	20.59	19.01
Rem.	--	--	0.20	--	0.09	--
Total:	100.00	100.00	100.67	100.00	100.72	99.76

Alteration Products:

Erythrite $Co_3As_2O_8.8H_2O$

(49) Name: Gudmundite

Formula: FeSbS

Typical Analyses:

Fe	26.63	26.79
Ni	--	trace
Sb	58.08	57.31
S	15.29	15.47
Total:	100.00	99.57

(50) Name: Lautite

Formula: CuAsS

Typical Analyses:

Cu	37.28	36.10	37.07
As	43.92	45.66	44.53
S	18.80	17.88	18.30
Total:	100.00	99.64	99.90

(51) Name: Molybdenite

Formula: MoS_2

Typical Analyses:

Mo 59.94, S 40.06, Total 100.00

Most analyses show no other constituents. Ge has been found spectroscopically.

Alteration Products:

Ferrimolybdite $Fe_2O_3.3MoO_3.8H_2O$, powellite $Ca(Mo, W)O_4$, ilsemannite $Mo_3O_8.nH_2O$ (?)

(52) Name: Tungstenite

Formula: WS_2

Typical Analyses:

The only analysis available is based on impure material calculated to contain about 60 percent WS_2.

(53) Name: Polybasite

Formula: $(Ag, Cu)_{16}Sb_2S_{11}$

Typical Analyses:

Ag	74.32	68.90	67.95	64.49	57.96
Cu	--	5.21	6.07	9.70	12.52
Sb	10.49	8.85	5.15	8.08	5.36
As	--	1.07	3.88	1.78	4.60
S	15.19	15.33	16.37	15.10	17.45
Rem.	--	0.09	0.76	0.75	2.11
Total:	100.00	99.45	100.18	99.90	100.00

(54) Name: Pearceite

Formula: $Ag_{16}As_2S_{11}$

Typical Analyses:

Ag	77.46	72.43	63.54	59.73	59.22	56.90	55.17
Cu	--	3.04	10.70	12.91	15.65	14.85	18.11
Sb	--	0.25	0.43	0.18	--	0.30	--
As	6.72	6.23	7.29	6.29	7.56	7.01	7.39
S	15.82	16.83	17.07	17.73	17.46	18.13	17.71
Rem.	--	0.92	0.60	3.16	--	2.81	1.47
Total:	100.00	99.70	99.63	100.00	99.89	100.00	99.85

(55) Name: Argyrodite Formula: Ag_8GeS_6

Name: Canfieldite Formula: Ag_8SnS_6

Typical Analyses:

Ag	76.51	75.67	74.72	75.55	76.05	73.49	74.10
Ge	6.44	6.55	6.93	6.64	6.55	--	1.82
Sn	--	0.10	--	--	--	10.14	6.94
S	17.05	17.15	17.13	16.97	17.04	16.37	16.22
Fe	--	3.03	0.66)	0.24	0.13	--	0.21
Zn	--	0.11	0.22)			--	--
Rem.	--	0.34	--	0.34	0.29	--	--
Total:	100.00	99.95	99.66	99.74	100.06	100.00	99.29

(56) Name: Stephananite

Formula: Ag_5SbS_4

Typical Analyses:

Ag	68.33	68.65	68.36	68.33	68.30	68.25	68.21
Sb	15.42	15.22	15.30	15.26	15.00	15.20	15.86
S	16.25	16.02	16.33	16.41	16.70	16.55	15.95
Total:	100.00	99.89	99.99	100.00	100.00	100.00	100.02

Alteration Products:

native silver Ag

(57) Name: Pyrargyrite

Formula: Ag_3SbS_3

Typical Analyses:

Ag	59.76	59.75	60.04	59.91	60.17	60.21	60.07
Sb	22.48	22.45	22.39	22.09	21.64	20.69	21.20
As	--	--	0.27	0.12	0.52	1.02	0.79
S	17.76	17.81	17.74	17.79	17.65	17.78	17.89
Total:	100.00	100.01	100.44	99.91	99.98	99.70	99.95

Alteration Products:

Argentite Ag_2S, native silver Ag, cerargyrite AgCl, stibnite Sb_2S_3.

(58) Name: Proustite

Formula: Ag_3AsS_3

Typical Analyses:

Ag	65.42	64.12	64.65	65.10	65.38	65.06	64.50
Sb	--	0.08	trace	--	0.26	1.41	3.62
As	15.14	15.90	15.25	15.03	14.89	13.85	12.54
S	19.44	19.28	20.18	19.52	19.31	19.64	19.09
Rem.	--	0.75	0.70	--	--	--	--
Total:	100.00	100.13	100.78	99.65	99.84	99.96	99.75

Alteration Products:

Argentite Ag_2S, native silver Ag, cerargyrite AgCl, orpiment As_2S_3.

(59) Name: Pyrostilpnite

Formula: Ag_3SbS_3 (see pyrargyrite)

Typical Analyses:

Ag	59.76	59.44
Sb	22.48	22.30
S	17.76	18.11
Total:	100.00	99.85

(60) Name: Xanthoconite

Formula: Ag_3AsS_3 (see proustite)

Typical Analyses:

Ag	65.42	65.15	64.07
As	15.14	14.63	14.98
S	19.44	19.07	14.99
Total:	100.00	98.85	94.04

(61) Name: Wittichenite

Formula: Cu_3BiS_3

Typical Analyses:

Cu	38.46	36.22	36.76
Ag	--	--	0.15
Fe	--	--	0.35
Zn	--	--	0.13
Bi	42.15	44.34	41.13
Sb	--	--	0.41
As	--	--	0.79
S	19.39	19.44	20.30
Total:	100.00	100.00	100.02

Alteration Products:

Easy alteration to: covellite CuS, malachite $CuCO_3.Cu(OH)_2$, also bismuth oxide.

(62) Name: Tetrahedrite Formula: $(Cu, Fe)_{12}Sb_4S_{13}$

Name: Tennantite Formula: $(Cu, Fe)_{12}As_4S_{13}$

Typical Analyses:

Cu	45.77	37.75	37.42	33.39	40.57	39.16	32.76	44.50	51.57
Fe	--	1.10	6.60	4.64	4.53	2.00	1.46	0.62	--
Zn	--	6.51	1.72	3.53	1.61	4.87	0.38	7.28	--
Ag	--	0.11	--	4.86	0.03	trace	1.51	0.02	--
Hg	--	--	--	--	1.52	--	13.71	--	--
Pb	--	0.71	trace	--	--	--	trace	0.35	--
Ni	--	--	0.23	trace	--	--	--	--	--
Co	--	--	--	--	--	0.23	--	--	--
Bi	--	0.53	--	0.34	--	--	trace	--	--
Sb	29.22	28.66	29.28	25.22	20.60	25.71	27.90	trace	--
As	--	--	trace	1.46	5.07	1.68	0.84	18.76	20.26
S	25.01	24.61	25.70	25.74	25.21	24.48	20.60	27.58	28.17
Rem.	--	--	--	--	0.75	1.08	0.18	0.26	--
Total:	100.00	99.98	100.95	99.18	99.89	99.21	99.34	99.37	100.00

Alteration Products:

Malachite $CuCO_3.Cu(OH)_2$, azurite $2CuCO_3.Cu(OH)_2$, bindheimite (a hydrous antimonate of lead), cuprite Cu_2O, limonite $Fe_2O_3.nH_2O$, chrysocolla $CuSiO_3.2H_2O$, pitticite $Fe_2(AsO_4)(SO_4)(OH).nH_2O$, erythrite $Co_3As_2O_8.8H_2O$, sometimes earthly cinnabar HgS.

(63) Name: Sulvanite

Formula: Cu_3VS_4

Typical Analyses:

Cu	51.47	47.97	51.20	52.27
V	13.85	12.15	14.20	13.59
S	34.68	31.66	34.60	34.14
Rem.	--	7.49	--	--
Total:	100.00	99.27	100.00	100.00

(64) Name: Germanite

Formula: (Cu, Ge)(S, As)

Typical Analyses:

Pb	0.69	0.96	0.66	0.26
Cu	45.40	42.12	45.39	39.44
Ge	6.20	10.19	8.70	7.04
Ga	--	1.85	0.76	--
Fe	7.22	7.80	4.56	10.70
Zn	2.61	3.93	2.58	3.56
As	5.03	1.37	4.13	4.86
S	31.34	31.27	30.65	31.44
SiO_2	0.75	--	0.23	1.68
Rem.	--	--	1.89	--
Total:	99.24	99.49	99.55	98.98

(65) Name: Colusite

Formula: $Cu_3(As, Sn, V, Fe, Te)S_4$

Typical Analyses:

Cu	47.67	47.99	46.9
Fe	1.05	1.09	3.6
Sn	6.45	6.71	5.8
V	2.20	2.28	--
Te	1.21	1.26	0.4
Sb	0.19	0.19	0.64
As	9.18	9.54	8.4
S	32.05	30.65	29.2
Rem.	--	--	0.9
Total:	100.00	99.71	95.84

(66) Name: Famatinite

Formula: Cu_3SbS_4

Typical Analyses:

Cu	43.27	44.72	47.93	45.43	43.48	44.8
Fe	--	0.67	--	0.67	1.65	3.2
Sb	27.63	21.44	12.74	12.74	12.65	11.3
As	--	3.84	8.88	9.09	9.90	10.2
S	29.10	29.40	30.45	31.01	31.90	30.5
Rem.	--	0.59	--	0.65	0.288	--
Total:	100.00	100.66	100.00	99.59	99.86	100.00

Alteration Products:

Enargite (?) Cu_3AsS_4

(67) Name: Enargite

Formula: Cu_3AsS_4

Typical Analyses:

Cu	48.42	47.96	49.00	48.67	48.16	45.70
Fe	--	1.22	--	0.33	0.14	2.49
Zn	--	0.57	--	0.10	trace	0.17
Sb	--	--	1.54	1.76	1.93	5.04
As	19.02	18.16	15.88	17.91	17.53	14.02
S	32.56	32.21	33.23	31.44	32.34	32.74
Rem.	--	--	--	0.11	0.08	--
Total:	100.00	100.12	99.65	100.32	100.18	100.16

Alteration Products:

Tennantite $(Cu, Fe)_{12}As_4S_{13}$

May afford on oxidation a wide variety of copper arsenates; also alters to arsenic oxide.

(68) Name: Beegerite

Formula: $Pb_6Bi_2S_9$

Typical Analyses:

Pb	63.76	64.23	63.00	45.87	50.16
Ag	--	--	0.02	9.98	15.40
Cu	--	1.70	--	1.12	--
Bi	21.44	20.59	22.15	19.35	19.81
S	14.80	14.97	14.28	16.39	14.63
Rem.	--	--	--	3.01	--
Total:	100.00	101.49	99.45	95.72	100.00

(69) Name: Samsonite

Formula: $Ag_4MnSb_2S_6$

Typical Analyses:

Ag	46.79	45.95
Mn	5.96	5.86
Sb	26.40	26.33
S	20.85	20.55
Cu	--	0.18
Fe	--	0.22
$CaCO_3$	--	0.44
$MgCO_3$	--	0.46
Total:	100.00	99.86

(70) Name: Geocronite

Formula: $Pb_5(Sb, As)_2S_8$

Typical Analyses:

Pb	69.92	70.02	68.97	68.49	64.89	57.95	67.58
Cu	--	trace	--	--	1.60	5.93	--
Sb	8.07	7.78	9.20	9.13	16.00	17.33	15.67
As	5.05	4.47	4.49	4.59	--	--	--
S	17.26	17.57	17.23	17.20	16.90	17.73	16.73
Rem.	--	--	--	--	--	0.11	--
Total:	100.00	99.84	99.89	99.41	99.39	99.05	100.00

(71) Name: Gratonite

Formula: $Pb_9As_4S_{15}$

Typical Analyses:

Pb	70.49	71.12	70.79
As	11.33	10.82	10.60
Sb	--	0.21	0.08
S	18.18	17.38	18.01
Rem.	--	0.39	--
Total	100.00	99.92	99.48

(72) Name: Lengenbachite

Formula: $Pb_6(Ag, Cu)_2As_4S_{13}$

Typical Analyses:

Sb	58.13	57.89
Ag	5.93	5.64
Cu	2.44	2.36
Fe	--	0.17
Sb	--	0.77
As	14.01	13.46
S	19.49	19.33
Total:	100.00	99.62

(73) Name: Jordanite

Formula: possibly $Pb_{14}As_7S_{24}$

Typical Analyses:

Pb	69.20	68.72	68.67	70.80	70.19	68.80	69.56
As	12.46	12.39	12.46	9.90	11.37	12.40	10.32
S	18.34	18.31	18.81	17.06	18.22	18.24	19.44
Rem.	--	--	--	1.87	--	--	0.45
Total:	100.00	99.42	99.94	99.63	99.78	99.53	99.77

(74) Name: Guitermanite

Formula: $Pb_{10}As_6S_{19}$

Typical Analyses:

Pb	65.99	64.32
Cu	0.19	--
Fe	--	1.61
As	14.33	13.85
S	19.49	19.76
Total:	100.00	99.54

(75) Name: Meneghinite

Formula: $Pb_{13}Sb_7S_{23}$

Typical Analyses:

Pb	62.88	61.47	59.21	62.45	60.09
Cu	--	0.39	3.54	1.21	1.56
Fe	--	0.23	0.35	0.07	0.25
Sb	19.91	18.37	19.28	18.94	19.11
S	17.21	16.97	17.52	17.47	18.22
Rem.	--	0.82	--	0.05	--
Total:	100.00	98.25	99.90	100.19	99.23

(76) Name: Lillianite

Formula: $Pb_3Bi_2S_6$

Typical Analyses:

Pb	50.46	47.62	48.21	48.05
Cu	--	0.20	1.12	0.69
Fe	--	0.47	--	0.16
Bi	33.93	34.60	34.36	33.84
Sb	--	--	--	--
Se	--	0.35	--	--
S	15.61	15.89	15.79	15.92
Rem.	--	0.83	--	0.50
Total:	100.00	99.96	99.48	99.16

(77) Name: Bournonite

Formula: $PbCuSbS_3$

Typical Analyses:

Pb	42.40	43.18	42.34	42.75	43.25
Fe	--	--	0.27	--	--
Ag	--	--	--	trace	--
Zn	--	--	0.04	--	--
Cu	13.01	13.14	12.80	12.77	12.86
Sb	24.91	25.03	24.44	24.76	24.53
As	--	--	--	--	--
S	19.68	19.59	19.58	19.40	19.17
Rem.	--	--	0.37	--	--
Total:	100.00	100.94	99.84	99.68	99.81

Alteration Products:

Bindheimite ($Pb_2Sb_2O_6(O,OH)$), antimony oxides, cerussite $PbCO_3$, malachite $CuCO_3.Cu(OH)_2$, azurite $2CuCO_3.Cu(OH)_2$, linarite

(78) Name: Seligmannite

Formula: $PbCuAsS_3$

Typical Analyses:

Pb	46.89	46.34
Fe	--	0.06
Zn	--	0.27
Ag	--	0.11
Cu	14.38	13.09
Sb	--	0.64
As	16.99	16.88
S	21.74	21.73
Total:	100.00	99.12

(79) Name: Aikinite

Formula: $PbCuBiS_3$

Typical Analyses:

Pb	35.98	35.15	36.01
Cu	11.03	11.11	10.90
Bi	36.29	36.25	36.20
S	16.70	16.56	16.60
Total:	100.00	99.07	99.71

Alteration Products:

To a bismuth ocher, probably largely bismutite, malachite $CuCO_3.Cu(OH)_2$.

(80) Name: Berthonite

Formula: $Pb_2Cu_7Sb_5S_{13}$

Typical Analyses:

Pb	21.98	21.83
Cu	23.61	23.68
Sb	32.30	32.45
S	22.11	22.17
Total:	100.00	100.13

Alteration Products:

Chrysocolla $CuSiO_3.2H_2O$, malachite $CuCO_3.Cu(OH)_2$, cerussite $PbCO_3$, bindheimite ($Pb_2Sb_2O_6(O,OH)$)

(81) Name: Diaphorite

Formula: $Pb_2Ag_3Sb_4S_8$

Typical Analyses:

Pb	30.48	28.67	31.06
Ag	23.78	23.44	23.36
Sb	26.87	26.43	25.92
S	18.87	20.18	18.51
Rem.	--	1.40	--
Total:	100.00	100.12	98.85

(82) Name: Freieslebenite

Formula: $Pb_3Ag_5Sb_5S_{12}$

Typical Analyses:

Pb	28.85	31.90	31.38	30.77	30.08	30.00
Ag	25.03	22.45	23.31	23.08	23.76	22.18
Sb	28.26	26.83	25.64	27.11	27.05	27.72
S	17.86	17.60	18.90	18.41	18.71	18.77
Rem.	--	--	0.13	0.63	--	1.33
Total:	100.00	98.78	99.36	100.00	99.60	100.00

(83) Name: Klaprothite

Formula: $Cu_6Bi_4S_9$

Typical Analyses:

Bi	55.51	53.87	53.21	51.62	51.40
Cu	25.33	23.96	24.91	30.48	28.82
Fe	--	1.70	--	trace	0.91
S	19.16	18.66	18.12	17.64	18.69
Rem.	--	--	1.16	--	--
Total:	100.00	98.19	97.40	99.74	99.82

Alteration Products:

Malachite $CuCO_3.Cu(OH)_2$, bismutite

(84) Name: Boulangerite

Formula: $Pb_5Sb_4S_{11}$

Typical Analyses:

Pb	50.57	51.00	53.33	54.34	54.44	55.05	55.08
Sb	29.49	27.82	24.67	25.33	24.55	25.71	24.38
S	19.91	18.99	18.11	18.51	18.98	18.82	18.65
Rem.	--	2.54	2.11	0.83	1.50	0.25	1.10
Total:	99.97	100.35	98.22	99.01	99.47	99.83	99.21

Alteration Products:

Bindheimite $(Pb_2Sb_2O_6(O,OH))$

(85) Name: Owyheeite

Formula: $Pb_5Ag_2Sb_6S_{15}$

Typical Analyses:

Pb	42.18	40.77	43.86
Ag	8.80	7.40	6.14
Cu	--	0.75	1.55
Fe	--	0.46	0.05
Sb	29.41	30.61	29.26
S	19.61	20.81	19.06
Total:	100.00	100.80	99.92

(86) Name: Schirmerite

Formula: $PbAg_4Bi_4S_9$

Typical Analyses:

Ag	24.47	24.75	22.82
Pb	11.75	12.76	12.69
Bi	47.41	47.27	46.91
S	16.37	15.02	14.41
Rem.	--	0.20	0.11
Total:	100.00	100.00	96.94

(87) Name: Miargyrite

Formula: $AgSbS_2$

Typical Analyses:

Fe	--	--	trace	0.56	1.0	0.19
Cu	--	--	--	0.02	2.6	0.51
Pb	--	--	--	0.95	0.6	4.01
Ag	36.72	37.06	36.71	36.20	33.9	32.77
Sb	41.45	41.13	41.15	42.46	40.5	40.68
As	--	0.79	--	trace	trace	--
S	21.83	21.50	21.68	19.27	21.9	21.80
Rem.	--	--	--	0.80	--	--
Total:	100.00	100.48	99.54	100.26	100.5	99.96

(88) Name: Aramayoite

Formula: $Ag(Sb, Bi)S_2$

Typical Analyses:

Ag	34.77	34.74
Cu	--	0.53
Bi	14.02	13.75
Sb	30.55	29.95
S	20.66	20.87
Total:	100.00	99.84

(89) Name: Matildite

Formula: $AgBiS_2$

Typical Analyses:

Ag	28.33	28.76	26.39	21.86
Bi	54.84	54.50	52.89	58.50
S	16.83	17.24	16.66	16.28
Rem.	--	--	4.06	3.36
Total:	100.00	100.00	100.00	100.00

(90) Name: Smithite

Formula: $AgAsS_2$

Typical Analyses:

Ag	43.69	43.9
As	30.34	28.9
Sb	--	0.4
S	25.97	26.0
Total:	100.00	99.2

(91) Name: Chalcostibite

Formula: $CuSbS_2$

Typical Analyses:

Cu	25.48	26.20	24.72
Sb	48.81	48.60	48.45
S	25.71	25.20	26.20
Rem.	--	1.00	--
Total:	100.00	101.00	99.37

(92) Name: Emplectite

Formula: $CuBiS_2$

Typical Analyses:

Cu	18.88	18.80
Bi	62.08	61.95
S	19.04	19.16
Total:	100.00	99.91

Alteration Products:

Bismite (?)

(93) Name: Lorandite

Formula: $TlAsS_2$

Typical Analyses:

Tl	59.46	59.40	59.76	58.75	59.08
As	21.87	21.60	22.30	21.65	21.32
S	18.67	19.00	18.99	19.26	18.75
Rem.	--	--	--	0.08	0.12
Total:	100.00	100.00	101.65	99.74	99.27

(94) Name: Teallite

Formula: $PbSnS_2$

Typical Analyses:

Pb	53.05	52.98	52.09
Fe	--	0.20	0.17
Sn	30.51	30.39	30.55
S	16.44	16.29	16.91
Total:	100.00	99.86	99.72

Alteration Products:

Cassiterite SnO_2, franckeite $Pb_5Sn_3Sb_2S_{14}$. Also to various oxidized lead and zinc minerals.

(95) Name: Benjaminite

Formula: $Pb(Cu, Ag) Bi_2S_4$?

Typical Analyses:

Pb	24.91	25.18
Cu	5.10	4.69
Ag	4.32	3.51
Bi	50.25	50.78
S	15.42	15.84
Total:	100.00	100.00

(96) Name: Hammarite

Formula: $Pb_2Cu_2Bi_4S_9$

Typical Analyses:

Pb	24.87	27.40
Cu	7.63	7.60
Bi	50.18	47.59
S	17.32	17.01
Insol.	--	0.04
Total:	100.00	99.64

(97) Name: Dufrenoysite

Formula: $Pb_2As_2S_5$

Typical Analyses:

Pb	57.20	57.42	57.38
As	20.68	20.89	21.01
S	22.12	22.55	21.94
Total:	100.00	100.86	100.33

(98) Name: Cosalite

Formula: $Pb_2Bi_2S_5$

Typical Analyses:

Pb	41.75	39.55	38.68	37.88	37.68	36.23	34.54
Cu	--	2.71	2.02	1.24	3.41	3.41	1.19
Ag	--	--	--	1.67	0.32	1.50	0.82
Fe	--	0.25	--	1.79	0.68	0.19	--
Bi	42.10	40.21	42.38	39.21	41.75	42.34	46.44
S	16.15	17.20	16.59	15.76	15.92	16.33	17.01
Rem.	--	0.78	--	2.46	--	--	-
Total:	100.00	100.70	99.67	100.01	99.76	100.00	100.00

Alteration Products:

Bismutite

(99) Name: Kobellite

Formula: $Pb_2(Bi, Sb)_2S_5$

Typical Analyses:

Pb	44.37	40.74	38.95
Cu	--	0.88	0.97
Bi	29.87	28.37	30.61
Sb	8.57	9.38	8.13
S	17.19	18.61	17.76
Rem.	--	2.02	3.58
Total:	100.00	100.00	100.00

(100) Name: Franckeite

Formula: $Pb_5Sn_3Sb_2S_{14}$

Typical Analyses:

Pb	49.71	50.57	48.02	46.23	46.11	49.80
Fe	--	2.48	2.74	2.69	2.55	--
Zn	--	1.22	--	0.57	0.79	--
Ag	--	--	0.99	0.97	0.88	0.94
Sn	17.09	12.34	13.89	17.05	16.08	17.36
Sb	11.69	10.51	13.06	11.56	10.98	11.87
S	21.51	21.04	20.82	21.12	21.14	19.28
Rem.	--	0.71	--	--	0.72	--
Total:	100.00	98.87	99.52	100.19	99.25	99.25

(101) Name: Fizelyite

Formula: $Pb_5Ag_2Sb_8S_{18}$?

Typical Analyses:

Pb	36.96	37.48
Ag	7.70	7.70
Fe	--	0.62
Sb	34.75	34.02
As	--	0.32
S	20.59	20.10
Insol.	--	0.30
Total:	100.00	100.54

(102) Name: Ramdohrite

Formula: $Pb_3Ag_2Sb_6S_{13}$

Typical Analyses:

Pb	31.32	30.6	30.3
Fe	--	n.d.	0.3
Cu	--	0.3	0.3
Ag	10.87	9.6	10.1
Sb	36.81	32.8	31.1
Bi	--	n.d.	2.5
S	21.00	20.4	20.1
Rem.	--	6.6	5.5
Total:	100.00	100.3	100.2

(103) Name: Wittite

Formula: $Pb_5Bi_6(S, Se)_{14}$?

Typical Analyses:

Pb	35.98	33.85
Bi	43.55	43.33
S	12.25	12.14
Se	8.22	8.46
Ag	--	0.19
Cu	--	0.08
Fe	--	0.28
Zn	--	0.26
Insol.	--	0.54
Total:	100.00	99.13

(104) Name: Jamesonite

Formula: $Pb_4FeSb_6S_{14}$

Typical Analyses:

Pb	40.16	42.79	40.47	40.32	40.14	40.08	39.97	39.05
Fe	2.71	2.83	2.68	3.68	2.64	2.79	3.63	2.00
Cu	--	1.01	0.50	--	0.18	0.22	--	3.45
Sb	35.39	31.94	n.d.	32.92	34.25	34.70	32.62	32.00
S	21.74	20.86	21.35	21.40	22.34	21.37	21.78	21.75
Rem.	--	1.84	5.82	1.24	--	0.13	1.48	2.16
Total:	100.00	101.27	70.82	99.56	99.55	99.29	99.48	100.41

Alteration Products:

Bindheimite ($Pb_2Sb_2O_6(O,OH)$), also to ill-defined antimony ochres.

(105) Name: Rathite

Formula: $Pb_{13}As_{18}S_{40}$

Typical Analyses:

Pb	50.59	51.51	51.62	52.43	52.98
Fe	--	--	--	0.33	0.56
As	25.32	24.62	24.91	21.96	17.21
Sb	--	--	--	0.43	4.53
S	24.09	23.41	23.62	24.11	23.72
Total:	100.00	99.54	100.15	99.26	99.00

Alteration Products:

Said to alter along cleavages and twin lamellae to baumhauerite $Pb_4As_6S_{13}$ and other arsenic sulphides.

(106) Name: Andorite

Formula: $PbAgSb_3S_6$

Typical Analyses:

Pb	23.75	24.10	21.81	25.06	22.25
Ag	12.36	10.94	11.73	12.98	10.90
Cu	--	0.68	0.73	--	0.96
Fe	--	0.30	1.45	--	0.75
Sb	41.87	41.31	41.76	40.41	40.75
S	22.02	22.06	22.19	21.55	24.26
Rem.	--	--	--	--	0.31
Total:	100.00	99.39	99.67	100.00	100.18

Alteration Product:

An unidentified fibrous sulphantimonide of lead and silver.

(107) Name: Lindstromite

Formula: $PbCuBi_3S_6$

Typical Analyses:

Pb	19.05	18.95
Cu	5.85	5.84
Fe	--	tr.
Bi	57.40	57.13
S	17.70	17.88
Insol.	--	0.20
Total:	100.00	100.00

(108) Name: Baumhauerite

Formula: $Pb_4As_6S_{13}$

Typical Analyses:

Pb	48.90	48.86
As	26.51	26.42
S	24.59	24.39
Total:	100.00	99.67

(109) Name: Fuloppite

Formula: $Pb_3Sb_8S_{15}$

Typical Analyses:

Pb	29.93	28.29
Sb	46.91	49.90
S	23.16	24.10
Rem.	--	0.19
Total:	100.00	100.08

(110) Name: Plagionite

Formula: $Pb_5Sb_8S_{17}$

Typical Analyses:

Pb	40.55	41.24	40.28	44.20
Sb	38.12	37.35	38.30	34.40
S	21.33	21.10	21.43	20.70
Rem.	--	--	0.18	1.22
Total:	100.00	99.69	100.19	100.52

Alteration Products:

Kermesite Sb_2S_2O

(111) Name: Heteromorphite

Formula: $Pb_7Sb_8S_{19}$

Typical Analyses:

Pb	47.81	47.86	48.89	48.48
Zn	--	0.60	0.18	--
Sb	32.11	31.20	31.08	32.98
S	20.08	19.90	19.36	20.32
Rem.	--	--	0.10	--
Total:	100.00	99.56	99.61	101.78

(112) Name: Semseyite

Formula: $Pb_9Sb_8S_{21}$

Typical Analyses:

Pb	53.10	54.27	53.21	52.9	52.49	52.37	51.88	51.84
Sb	27.73	26.17	26.95	24.8	28.34	25.49	27.20	28.62
S	19.17	18.99	19.90	18.7	18.93	18.81	19.73	19.42
Rem.	--	0.26	0.08	1.6	0.46	3.14	1.82	--
Total:	100.00	99.69	100.14	98.0	100.22	99.81	100.63	99.88

(113) Name: Hutchinsonite

Formula: $(Pb, Tl)_2\ (Cu, Ag)As_5S_{10}$?

Typical Analyses:

Pb	12½	16
Tl	25	18
Ag	9	2
Cu	-	3
Fe	-	½
As	30½	29½
Sb	-	2
S	26	26½
Total:	103	97½

(114) Name: Rezbanyite

Formula: $Pb_3Cu_2Bi_{10}S_{19}$

Typical Analyses:

Pb	18.03	18.24
Cu	3.69	4.13
Fe	--	0.44
Bi	60.62	59.25
S	17.66	17.86
Rem.	--	0.06
Total:	100.00	99.98

(115) Name: Galenobismutite

Formula: $PbBi_2S_4$

Typical Analyses:

Pb	27.50	27.18	27.65	23.93	31.33	33.02
Fe	--	trace	trace	0.39	0.27	--
Cu	--	--	--	1.73	--	--
Sb	--	--	--	2.56	0.19	3.05
Bi	55.48	54.13	54.69	53.59	51.25	46.83
S	17.02	16.78	17.35	17.80	17.16	17.10
Total:	100.00	98.09	99.69	100.00	100.20	100.00

(116) Name: Weibullite

Formula: $PbBi_2(S, Se)_4$

Typical Analyses:

Pb	25.15	27.88	25.37
Ag	--	0.33	--
Bi	50.74	49.88	51.24
Se	14.38	12.43	14.03
S	9.73	9.75	9.36
Total:	100.00	100.27	100.00

(117) Name: Platynite

Formula: $PbBi_2 (Se, S)_3$

Typical Analyses:

Pb	25.44	26.45
Bi	51.16	50.22
Se	19.45	19.20
S	3.95	4.13
Total:	100.00	100.00

(118) Name: Chiviatite

Formula: $Pb_3Bi_8S_{15}$?

Typical Analyses:

Pb	22.41	16.73	17.39
Cu	--	2.42	1.20
Fe	--	1.02	0.29
Ag	--	trace	0.15
Bi	60.26	60.95	56.72
S	17.33	18.00	11.48
Se	--	--	12.28
Rem.	--	0.59	0.57
Total:	100.00	99.71	100.04

(119) Name: Alaskaite

Formula: $Pb(Ag, Cu)_2Bi_4S_8$?

Typical Analyses:

Pb	13.95	14.41	15.4	11.79	12.02	19.02
Ag	9.68	9.07	11.7	8.74	7.80	3.26
Cu	2.85	2.68	1.6	3.46	5.11	4.07
Zn	--	--	--	0.79	0.34	0.22
Bi	56.26	56.11	55.3	56.97	53.39	55.81
S	17.26	17.73	16.0	17.63	17.98	17.62
Rem.	--	--	--	0.62	2.64	--
Total:	100.00	100.00	100.0	100.00	99.28	100.00

(120) Name: Zinkenite

Formula: $Pb_6Sb_{14}S_{27}$

Typical Analyses:

Pb	32.60	34.33	32.77	31.84	29.80	29.33
Cu	--	0.70	1.20	0.42	0.64	--
Fe	--	0.06	0.02	--	0.84	0.08
Sb	44.70	42.15	35.00	44.39	43.32	46.17
As	--	--	5.64	--	0.27	--
S	22.70	22.63	22.50	22.58	23.02	23.10
Rem.	--	--	1.58	--	2.54	0.94
Total:	100.00	99.87	98.71	99.23	100.43	99.62

Alteration Products:

Bindheimite ($Pb_2Sb_2O_6(O, OH)$)

(121) Name: Sartorite

Formula: $PbAs_2S_4$

Typical Analyses:

Pb	42.70	43.63	42.93	41.92
As	30.87	30.46	31.11	29.59
S	26.43	25.51	25.32	25.49
Rem.	--	--	--	0.04
Total	100.00	99.60	99.36	97.04

(122) Name: Berthierite

Formula: $FeSb_2S_4$

Typical Analyses:

Fe	13.21	13.43	13.42	13.38	12.61	13.54	10.09
Mn	--	--	--	--	0.31	--	3.56
Sb	56.55	56.06	57.02	57.44	55.96	56.11	56.61

S	30.24	29.46	29.56	29.18	29.28	30.12	29.12
Rem.	--	0.33	--	--	1.29	0.23	--
Total:	100.00	99.28	100.00	100.00	99.45	100.00	99.38

(123) Name: Cylindrite

Formula: $Pb_3Sn_4Sb_2S_{14}$

Typical Analyses:

Pb	34.76	35.41	35.24	34.58	36.74
Fe	--	3.00	2.81	2.77	--
Ag	--	0.62	0.50	0.28	0.41
Sb	13.61	8.73	12.31	12.98	13.32
Sn	26.54	26.37	25.65	25.10	26.71
S	25.09	24.50	23.83	23.88	22.79
Total:	100.00	98.63	100.34	99.59	99.97

Alteration Products:

Cassiterite SnO_2, cerussite $PbCO_3$.

(124) Name: Gladite

Formula: $PbCuBi_5S_9$

Typical Analyses:

Pb	12.92	12.40
Fe	--	0.19
Cu	3.96	3.98
Bi	65.14	64.96
S	17.98	18.08
Insol.	--	0.12
Total:	100.00	99.69

(125) Name: Livingstonite

Formula: $HgSb_4S_7$

Typical Analyses:

Hg	22.00	22.61	22.52
Sb	53.40	52.21	53.75
S	24.60	24.50	23.73
Rem.	--	0.68	--
Total:	100.00	100.00	100.00

Alteration Products:

Alters to a black material which apparently is a mixture of metacinnabar (Hg, Fe, Zn)S and antimony oxide.

A DETAILED LOOK AT THE IRON SULPHIDES

In the hardrock mining districts, iron sulphide occurs in three very common and very distinct forms:

(a) pyrite (isometric crystal system)

(b) marcasite (orthorhombic crystal system)

(c) pyrrhotite (hexagonal crystal system)

(a) Pyrite

Pyrite, a disulphide of iron (FeS_2), is an extremely common component of the sulphide ore bodies that are located in the Ontario hardrock mining districts. In fact, pyrite is the most widespread and most abundant of the many sulphide minerals known. It occurs under almost all conditions of mineral deposition and is therefore a leading example of the so-called "persistent" minerals.

Detailed chemical data concerning pyrite are given. in section #38 of "Sulphides and Sulphosalts" in this report. It is extremely important to note that, at least nickelian and cobaltian varieties of pyrite are known. In the nickelian variety, nickel (often with subordinate amounts of cobalt) substitutes for some of the iron in the FeS_2 lattice. Nickel to iron ratios of 1:1.84 are known. It is possible that a complete substitution series exists from pyrite (FeS_2) to bravoite $(Ni,Fe)S_2$. The substitution of nickel for iron is accompanied by a regular increase in the cell dimensions and by a decrease in hardness (with a hardness of

6 to 6.5, pyrite is one of the hardest sulphides known). An increasing content of nickel also causes the typical pyrite colour of pale brass-yellow to incline to silvery white, violet-grey and grey.

Similarly, the cobaltian variety of pyrite contains some cobalt in substitution for iron. Cobalt to iron ratios of 1:2.5 are known.

Characteristics of Pyrite

Cleavage - indistinct
Fracture - conchoidal to uneven
Tenacity - brittle
Luster - metallic, splendent to glistening
Streak - greenish black to brownish black
Shows both positive and negative thermoelectricity
Paramagnetic
Conducts electricity
Specific gravity 5.013 - 5.018

(b) Marcasite

Like pyrite, marcasite is a disulphide of iron (FeS_2). Marcasite is found most often in surface and near-surface deposits where it has been formed at relatively low temperatures and from acid solutions (under higher temperatures and conditions of low acidity or of alkalinity, the more stable form (pyrite) is deposited). Marcasite is in most instances, a supergene mineral, but may perhaps be deposited from low-temperature ascending vein solutions as one of the last minerals to form. Most frequently marcasite is found in sedimentary deposits such as limestone, clays and lignite.

Marcasite is known for its rapid rate of decomposition into ferrous sulphate and sulphuric acid. Specimens of marcasite sitting on a shelf in a normal room will, on occasion, revert to a crumbly grey-white mass of ferrous sulphate within a few weeks or a few months.

Detailed chemical data concerning marcasite is given in section #46 of "Sulphides and Sulphosalts" in this report.

Characteristics of Marcasite

Cleavage - rather distinct
Fracture - uneven
Tenacity - brittle
Hardness - 6 - 6½
Specific Gravity - 4.887
Luster - Metallic
Colour - pale bronze-yellow (deepening on exposure), tin-white on fresh fracture
Streak - greyish or brownish black

(c) Pyrrhotite

Pyrrhotite, intimately associated with pentlandite $(Fe,Ni)_9S_8$ and other sulphides, occurs principally in basic igneous rocks from which it may have been formed by magmatic segregation. Pyrrhotite is often found "massive" in association with other sulphides in veins and replacement bodies of the higher temperature type in which case it is often one of the earliest sulphide minerals to form.

Pyrrhotite has been given the formula $Fe_{1-x}S$ where x varies between 0 and 0.2. Troilite is a variety of pyrrhotite having a composition near FeS.

Detailed chemical data concerning pyrrhotite is given in section #23 of "Sulphides and Sulphosalts" in this report.

Characteristics of Pyrrhotite

Cleavage - none

Fracture - uneven to subconchoidal

Tenacity - brittle

Luster - metallic

Streak - dark greyish-black

Colour - bronze yellow to pinchbeck brown, tarnishing quickly on exposure, sometimes to irridescence

Magnetic but varying in intensity

Specific gravity - 4.58 to 4.65

Hardness - 3½ to 4½

The rates of reaction of pyrite, marcasite and pyrrhotite under typical acid mine drainage circumstances in hardrock mining districts are significantly different. It has been reported for instance that marcasite reacts nine times as fast as good quality pyrite. On the other hand, impure sulphide material (corresponding perhaps to poor quality pyrrhotite) is said to react up to eighty-one times as fast as good quality pyrite. These facts are interesting but they are really not too significant as far as the hardrock mining industry is concerned. Severe acid mine drainage problems are known to occur in Ontario where marcasite and pyrrhotite are, relatively speaking, absent. In addition, most sulphide tailings areas in Ontario contain intimate mixtures of two or more iron sulphide species.

SOLUBILITY CHARACTERISTICS OF SULPHIDES AND RELATED SUBSTANCES

The tailings mass generated by a sulphide mining operation consists essentially of finely divided silicates, oxides and sulphides. As such, some knowledge of the solubility of these substances is required in order to realistically assess a related environmental situation. In addition, the reactive mineral species in a tailings mass produce salts that may or may not be water soluble and hence may or may not escape the tailings area in solution. Again, knowledge relating to the solubility or relative solubility of these salts is essential.

Solubility Product Constants for Common Sulphides

Sulphide	Mineral Name	Solubility Product Constants
Cu_2S	Chalcocite	2.6×10^{-49}
Ag_2S	Argentite	5.9×10^{-52}
MgS		2.0×10^{-15}
MnS		1.1×10^{-15}
FeS		3.8×10^{-20}
CoS		3.1×10^{-23}
ZnS	Sphalerite	7.4×10^{-27}
SnS		1.0×10^{-27}
CdS	Greenockite	1.2×10^{-28}
PbS	Galena	6.8×10^{-29}
CuS		3.2×10^{-38}
HgS	Cinnabar	1.00×10^{-47}
Sb_2S_3	Stibnite	2.9×10^{-59}
Bi_2S_3	Bismuthinite	7.1×10^{-61}

Calculated solubility of metallic sulfides in water at pH 7 (grams MS per liter of solution)

Compound	25°C	100°C	200°C	300°C	400°C
ZnS	1.42x10^{-7}	3.6x10^{-4}	2.2x$^{10-2}$	8x10^{-1}	5.92
PbS	8.65x10^{-9}	8.9x10^{-8}	2.1x10^{-6}	1.6x10^{-5}	2.1x10^{-4}
CuS	2.4x10^{-13}	4.1x10^{-13}	4.6x10^{-12}	2.3x10^{-11}	7.8x10^{-11}
HgS	1.0x10^{-18}	2.2x10^{-17}	6.4x10^{-16}	5.6x10^{-15}	3.1x10^{-14}
Ag_2S	3.8x10^{-13}	5.7x10^{-13}	3.3x10^{-12}	1.4x10^{-11}	2.3x10^{-11}
Cu_2S	4.8x10^{-10}	4.0x10^{-11}	5.6x10^{-10}	2.6x10^{-9}	7.3x10^{-9}

Calculated solubility of CuS in water (moles CuS per liter of solution) versus pH

pH	25°C	50°C	75°C	200°C	400°C
1	2.3x10^{-16}	1.8x10^{-16}	2.0x10^{-16}	8.8x10^{-15}	4.4x10^{-13}
3	2.3x10^{-20}	1.8x10^{-20}	2.0x10^{-20}	8.8x10^{-19}	4.4x10^{-17}
5	2.3x10^{-24}	1.3x10^{-24}	2.0x10^{-24}	8.8x10^{-23}	4.4x10^{-21}
7	3.5x10^{-19}	1.6x10^{-18}	6.0x10^{-18}		
9	9.0x10^{-16}	3.6x10^{-15}	1.0x10^{-14}		
11	9.0x10^{-12}	3.6x10^{-11}	1.0x10^{-10}		
13	9.0x10^{-8}	3.6x10^{-7}	1.0x10^{-6}		

In strongly acid solutions (acid mine drainage circumstances), in which the simple metallic ion is (hypothetically) the only significant species containing the metal, the relative solubilities of the sulphides of the following metals can be placed in a series, starting with the most soluble:

Mn, Fe, Ni, Co, Zn, Cd, Pb, Cu(ous), Ag, Cu(ic), Bi, Hg

This is a very wide range, the ratio of the solubilities of the two ends being about 10^{23}.

In strongly alkaline sulphide solutions, the relative solubilities of the sulphides of some of the metals can be placed in an analogous order, parenthesis denoting general position of a group but no established order within the group starting with the least soluble:

(Fe, Zn, Cd, Pb, Cu), Ag, Bi (Hg, Au, Sb, As, Te)

Solubility Products

The numbers (given below) are negative logarithms of activity products at 25°C. For example, the number after $PbCl_2$ (below) is 4.8. This means that

$$\text{Solubility product for } PbCl_2 = (Pb^{++})(Cl^-)^2 = 10^{-4.8}$$

The physical state of the compounds is not in every case clear from the literature, but for the most part they are probably finely crystalline precipitates. Because of this uncertainty about physical state and because of differences in experimental methods, values in the literature show considerable disagreement.

(a) Carbonates

$BaCO_3$ (Witherite)	8.8
$CdCO_3$	11.3
$CaCO_3$ (Calcite)	8.35
$CaCO_3$ (Aragonite)	8.22
$CoCO_3$	12.8
$FeCO_3$ (Siderite)	10.5
$PbCO_3$	13.1
$MgCO_3$ (Magnesite)	5.1

$MgCO_3.3H_2O$ (Nesquehonite)	5.6
$MnCO_3$ (Rhodochrosite)	10.2
$NiCO_3$	6.9
$SrCO_3$ (Strontianite)	9.6
UO_2CO_3 $(UO_2^{++})(CO_3^{=})$	10.6
$ZnCO_3$ (at 20°C)	10.8
$Cu_2(OH)_2CO_3$ $(Cu^{++})^2(OH^-)^2(CO_3^{=})$ (Malachite)	33.8

(b) Chlorides

$AgCl$	9.8
$CuCl$	5.9
Hg_2Cl_2 $(Hg_2^{++})(Cl^-)^2$	17.9
$PbCl_2$	4.8

(c) Fluorides

BaF_2	5.9
CaF_2 (Fluorite)	10.5
MgF_2 (Sellaite)	8.2
SrF_2	8.6
PbF_2	7.5

(d) Sulphates

Ag_2SO_4 $(Ag^+)^2(SO_4^{=})$	4.8
$BaSO_4$ (Barite)	10.0
$CaSO_4$ (Anhydrite)	4.5
$CaSO_4.2H_2O$ (Gypsum)	4.6
$PbSO_4$ (Anglesite)	7.8
$SrSO_4$ (Celestite)	6.5

(e) Sulphides

Ag_2S (Argentite)	49.2
Bi_2S_3 (Bismuthinite)	96
CdS (Greenockite)	27.8
CoS (Alpha)	20.4
CoS (Beta)	24.7
CuS	36.1

Cu_2S $(Cu^+)^2(S^=)$	48.0
FeS	17.2
HgS (Metacinnabar)	51.8
HgS (Cinnabar)	52.4
MnS (Pink)	9.6
MnS (Green)	12.6
NiS (Alpha)	18.5
NiS (Gamma)	25.7
PbS (Galena)	27.5
Sb_2S_3 (Stibnite) $(Sb^{3+})^2(S^=)^3$	92.8
SnS	25.0
ZnS (Wurtzite)	21.6
ZnS (Sphalerite)	23.8

(f) Phosphates

$AlPO_4 \cdot 2H_2O$ (Variscite)	22.1
$CaHPO_4 \cdot 2H_2O$ $(Ca^{++})(HPO_4^=)$	6.6
$Ca_3(PO_4)_2$ $(Ca^{++})^3(PO_4^{3-})^2$	28.7
$Ca_5(PO_4)_3F$ (Fluorapatite)	60.4
$Ca_5(PO_4)_3OH$ $(Ca^{++})^5(PO_4^{3-})^3(OH^-)$ (Hydroxylapatite)	57.8
$Cu_3(PO_4)_2$	36.9
$FePO_4$ (Amorphous)	21.6
$FePO_4 \cdot 2H_2O$ (Strengite)	26.2
$Mg_3(PO_4)_2$ (at 38°C)	27.2
$PbHPO_4$	9.9
$Pb_3(PO_4)_2$ (at 38°C)	43.5
UO_2HPO_4 $(UO_2^{++})(HPO_4^=)$	12.2
$(UO_2)_3(PO_4)_2$	46.7
$Zn_3(PO_4)_2$ (at 18 to 20°C)	32.0

Solubility of Salts and Bases

NOTE: The number quoted in each case indicates the number of grams of the salt that can be dissolved at 25°C (unless otherwise indicated) in 100 mls. of water. All values are based on the anhydrous salt (unless otherwise indicated). Blank spaces indicate that data is not available or that the compound does not exist. Subscripts indicate the number of zeros before the first integer.

Abbreviations Used:

s = soluble

v.s. = very soluble

v. sl. s. = very slightly soluble

sl. s. = slightly soluble

ins. = practically insoluble

hydr. = hydrolyzed by water

dihd. = dihydrate

d. = decomposes

	Cu^{++}	Zn^{++}	Pb^{++}	Ag^{+}	Hg_2^{++}	Hg^{++}	Cd^{++}	Ni^{++}	Co^{++}	Mn^{++}
Cl^{-}	77.3	432	1.1	$0.0_{3}179$	$0.0_{4}38$	7.3	120.5	65.6	56.3	77.18
Br^{-}	126	471	0.9744	$0.0_{4}137$	$0.0_{5}4$	0.61	112	134	119.1	152
I^{-}	1.11	492^{22°	0.0764	2.8×10^{-7}	2×10^{-8}	0.00610	86.22	154	203	s.
NO_3^{-}	151	128	60.6	255.5	d.	v.s.	158	100	98.9^{18°	165.8
SO_4^{--}	22.7	57.45	0.00425	0.841	0.053	d.	76.60^{20°	$37.90^{22.6^\circ}$	38.9^{24°	64.78
CrO_4^{--}	ins.	ins.	$0.0_{5}58$	0.0043	v.sl.s.	sl.s.d.	ins.	ins.	ins.	
CO_3^{--}	ins.	0.0206	$0.0_{3}15^{20^\circ}$	0.0032	$0.0_{5}45$	ins.	ins.	0.00925	ins.	0.0065
$C_2H_3O_2^{-}$	7.28	30^{20°	55.2	1.12	0.102^{21°	25^{10°	v.s.	16.6	s.	64.5^{5° $(.4H_2O)$
OH^{-}	$0.0_{3}3$	$0.0_{6}26^{18^\circ}$	0.012	d.	v.sl.s.	ins.	$0.0_{3}26$	0.0013^{20°	$0.0_{3}32$	0.002^{30°
PO_4^{---}	ins.	ins.	$0.0_{4}135^{20^\circ}$	$0.0_{3}644^{20^\circ}$	ins.	ins.	ins.	ins.	ins.	
S^{--}	1.7×10^{-18}	3.4×10^{-11}	6.2×10^{-14}	1.0×10^{-16}		7×10^{-25}	1.4×10^{-13}	1.1×10^{-11}	2.9×10^{-13}	3.2×10^{-7}

	Na^+	**K^+**	**Mg^{++}**	**Ca^{++}**	**Sr^{++}**	**Ba^{++}**	**Fe^{++}**	**Fe^{+++}**
Cl^-	36.12	35.5	56.7	$74.5^{20°}$	55.8	37	64.5	$91.85^{20°}$
Br^-	94.59	67.7	103.3	153	107	106	$116.9^{21°}$	
I^-	184.2	148	$139.8^{20°}$	$208^{20°}$	$177.8^{20°}$	220.5		
NO_3^-	91-92	37.3	72.7	138.0	82.0	10.2	87	87.19
SO_4^{--}	28.0	12.04	36.43	0.208	$0.013^{20°}$	$0.0_3 26$	26.69	440
CrO_4^{--}	85.4	62.5	$72.3^{18°}$	2.38	0.091	$0.0_3 37^{20°}$		
CO_3^{--}	29.12	112.1	$0.0716^{15°}$	0.00153	$0.00109^{24°}$	$0.0024^{24.2°}$	0.0067	
$C_2H_3O_2^-$	$46.5^{20°}$	269.4	65.60	34.2	40.19	$78.1^{24.1°}$	v.s.	hydr.
OH^-	$109^{20°}$	118.5	$0.0_3 93$	0.12	$1.74^{20°}$ $(.8H_2O)$	4.68	$0.0_4 732$	$5.2x10^{-9}$
PO_4^{---}	14.0	sl.s.	0.0205 $(.4H_2O)$	0.001-0.010	ins.	ins.	ins.	ins.
S^{--}	hydr.	hydr.	hydr.	hydr.	hydr.	hydr.	$5.4x10^{-9}$	$6x10^{-17}$

References for this section:

"Semimicro Qualitative Analysis" by Evans, Garrett and Sisler, Revised Edition, Ginn and Company, 1951.

"Introduction to Geochemistry" by K. Krauskopf, McGraw-Hill Book Company, 1967.

THE CHEMISTRY OF ACID MINE DRAINAGE

Part A - Chemical

The following reactions are the basic chemical reactions that describe an acid mine drainage situation:

Reaction #1 (Sulphide to Sulphate)

When natural sulphuritic material in the form of a sulphide (and usually in combination with iron) is exposed to the atmosphere (oxygen), it may theoretically oxidize in two ways with water (or water vapour) as the limiting condition:

(a) Assuming that the process takes place in a dry environment, an equal amount of sulphur dioxide will be generated with the formation of (water soluble) ferrous sulphate:

$$FeS_2 + 3O_2 \text{ -----}\!> FeSO_4 + SO_2$$

(b) If, however, the oxidation proceeds in the presence of a sufficient quantity of water (or water vapour), then the direct formation of sulphuric acid and ferrous sulphate in equal parts results:

$$2FeS_2 + 2H_2O + 7O_2 \text{ -----}\!> 2FeSO_4 + 2H_2SO_4$$

In most mining environments (underground as well as in the tailings area), the above reaction is favoured.

Reaction #2 [Oxidation of Iron (Ferrous to Ferric)]

Ferrous sulphate in the presence of a sufficient quantity of sulphuric acid and oxygen oxidizes to the ferric state to form (water soluble) ferric sulphate:

$$4FeSO_4 + 2H_2SO_4 + O_2 \text{ -----}\!> 2Fe_2(SO_4)_3 + 2H_2O$$

Here water is not limiting since it is not a requirement for the reaction but rather is a product of the reaction.

Most evidence seems to indicate that a specific bacterium (T. ferrooxidans) is involved in the above reaction and is responsible for, at least, accelerating the oxidation of the ferrous iron to the ferric state.

Reaction #3 (Precipitation of Iron)

The ferric iron associated with the sulphate ion commonly combines with the hydroxyl $(OH)^-$ ion of water (HOH) to form ferric hydroxide. In an acid environment, ferric hydroxide is largely insoluble and accordingly precipitates:

$$Fe_2(SO_4)_3 + 6H_2O \text{ -----}\!> 2Fe(OH)_3 + 3H_2SO_4$$

IMPORTANT NOTE:

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion "backtriggers" the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \text{ -----}\!> 3FeSO_4 + 2S^o$$

$$S^o + 3O + H_2O \text{ -----}\!> H_2SO_4$$

The fact that very little 'free' sulphuric acid is found in mine waste drainage is probably due to the reactions between other soluble mineral species and sulphuric acid.

The above reactions are not as uncomplicated as they appear to be. Many "side" reactions can and do take place. For instance, it cannot be assumed that the reaction of ferrous sulphate, $FeSO_4$, to form ferric sulphate, $Fe_2(SO_4)_3$, is as simple as that outlined because, under certain conditions, a portion of the ferric sulphate formed may be precipitated as a relatively insoluble basic sulphate - that is, a sulphate containing Fe, SO_4, and OH.

Local deposits of various salts occur frequently as a result of pyrite decomposition in coal mining areas. The chemical nature of these salts provides important information with regard to the types of reactions that are carried to completion under acid mine drainage conditions. One of the most common salts that is readily apparent in both hard-rock and coal mining districts is ferrous sulphate. Ferrous sulphate is known in geology texts as the mineral melanterite ($FeSO_4.7H_2O$). Other hydration states of ferrous sulphate are also known to occur. A hydrated complex of ferrous hydroxy sulphate that is common in occurrence is known as the mineral copiapite ($(Fe(OH)_2.Fe_4(SO_4)_6.20H_2O)$). In other situations, white hair-like salts have been found in or near coal mine openings on gob and roof spall. Chemical and X-ray analyses have demonstrated that at least some of these salts are of the halotrichite-pickeringite series (halotrichite: $FeAl_2(SO_4)_4.22H_2O$; pickeringite: $MgAl_2(SO_4)_4.22H_2O$).

Under specific conditions, the oxidation of iron sulphides can result in the formation of partially oxidized sulphur compounds such as sulphite and thiosulphate. The oxidation of these materials yields polythionates and eventually sulphuric acid. The above species are all metastable in solution and oxidation appears to proceed along a chemical and biological route

$$S_2O_3 \dashrightarrow S_nO_6 \dashrightarrow S_3O_6 \dashrightarrow H_2SO_4$$

(thiosulphate) (polythionate) (trithionate) (sulphuric acid)

The thiosalts have been shown to be produced during the alkaline oxidation of various sulphide materials. In experiments conducted on New Brunswick ores, thiosalts were only formed at a pH greater than 7 and the concentration appeared to be a function of the hydroxyl ion concentration. In sulphide mine-mill operations, thiosalts are generated when alkaline solutions come into contact with sulphides (particularly iron sulphides). This happens almost continually during the process of froth flotation of sulphide ores. The following equation illustrates the possible mechanism involved in the dissolution process of sulphur from an iron sulphide mineral (in this case pyrrhotite) under alkaline flotation conditions:

$$Fe_7S_8 + 2OH^- \dashrightarrow 7FeS + S^= + H_2O + \tfrac{1}{2}O_2$$

The kinetics of oxidation of dissolved sulphide to sulphuric acid depend on many factors (which may include sunlight, water temperature, pH, and the presence of active sulphur oxidizing bacteria). The intermediate products of oxidation, called polythionates, further oxidize to sulphuric acid.

The oxidation of sulphide ion to thiosulphate ion proceeds as follows:

$$4S^{=} + 3O_2 \dashrightarrow 2S_2O_3^{=}$$

Polythionates, identified as $S_3O_6^{=}$, S_nO_6, (n, 4 to 8), are formed as shown below:

$$S_2O_3^{=} + H_2O + 4O \dashrightarrow 2SO_4^{=} + 2H^+$$

$$nS_2O_3^{=} + (n-2)H_2O + 2(5-n)O \dashrightarrow 2S_nO_6^{=} + 2(n-2)OH^-$$

and the oxidation to sulphuric acid is described as follows:

$$S_nO_6^{=} + (n-1)H_2O + (3n-5)O \dashrightarrow nSO_4^{=} + 2(n-1)H^+$$

This report deals almost exclusively with the type of acid mine drainage problem that results when naturally occurring inorganic sulphides undergo spontaneous decomposition. These sulphides are, in the sulphide mining industry, found as finely divided particles that form an inherent characteristic of the tailings areas serving the industry. In addition, the sulphides are found 'in situ' in mine workings. When the correct conditions are presented, the sulphide minerals oxidize to the corresponding metal ions plus the sulphate ion. Again, depending on whether or not the correct conditions are presented, the anions and cations released by sulphide decomposition may or may not gain access to local watercourses.

Iron, which is released as a result of iron sulphide decomposition, is one of the most common metals found in acid mine drainage flows. In fact, the ions of iron and their associations and reactions play a major role in the development and stabilization of acid mine drainage situations. Most acid mine drainage problems can be resolved only after the chemistry of iron has been studied in some detail.

The principal iron species which are found in mine water are believed to be Fe^{+2}, Fe^{+3}, $Fe(OH)_2(s)$, and $Fe(OH)_3(s)$.

Fe^{+2} is usually associated with the oxidation products of pyrite which have been leached from the mine or tailings area by ground water. The principal soluble oxidation product is $FeSO_4$. However, $FeSO_4$ hydrolyses and oxidizes to form various hydroxides, some of which are also soluble. Fe^{+2} in mine water is also associated with $FeCO_3$. Natural ground water leaching such minerals as siderite will contain Fe^{+2}. It is believed the $FeCO_3$ dissociates and ionizes and is in equilibrium with Fe^{+2}, $CO_3^{=}$, HCO_3^{-}.

Fe^{+3} in mine water occurs in solution under specific conditions. At low pH, < 3, Fe^{+3} is in solution. At higher pH, Fe^{+3} will be found in solution only as part of complexes formed with organic chelates, phosphates, and other anions. In the absence of chelating agents, Fe^{+3} should not be found in significant quantities in solution in mine drainage above pH 3.

Solubility of Iron - The principal iron species, Fe^{+2} and Fe^{+3}, form hydroxides which are insoluble. The solubility product, K_{sol}, for $Fe(OH)_2$ at 25 C in "slightly basic media" is 5.25×10^{-14}. The distribution of soluble Fe^{+2} and insoluble $Fe(OH)_2$ at various pH levels is shown in Figure 1, where percent composition is plotted versus pH. The factor limiting concentration of Fe^{+2} in solution is the equilibrium concentration at any pH. Table 1 gives the distribution of the various forms in which Fe^{+2} occurs at various pH levels.

FIGURE 1. DISTRIBUTION OF Fe^{+2} AND $Fe(OH)_2$ AS A FUNCTION OF pH

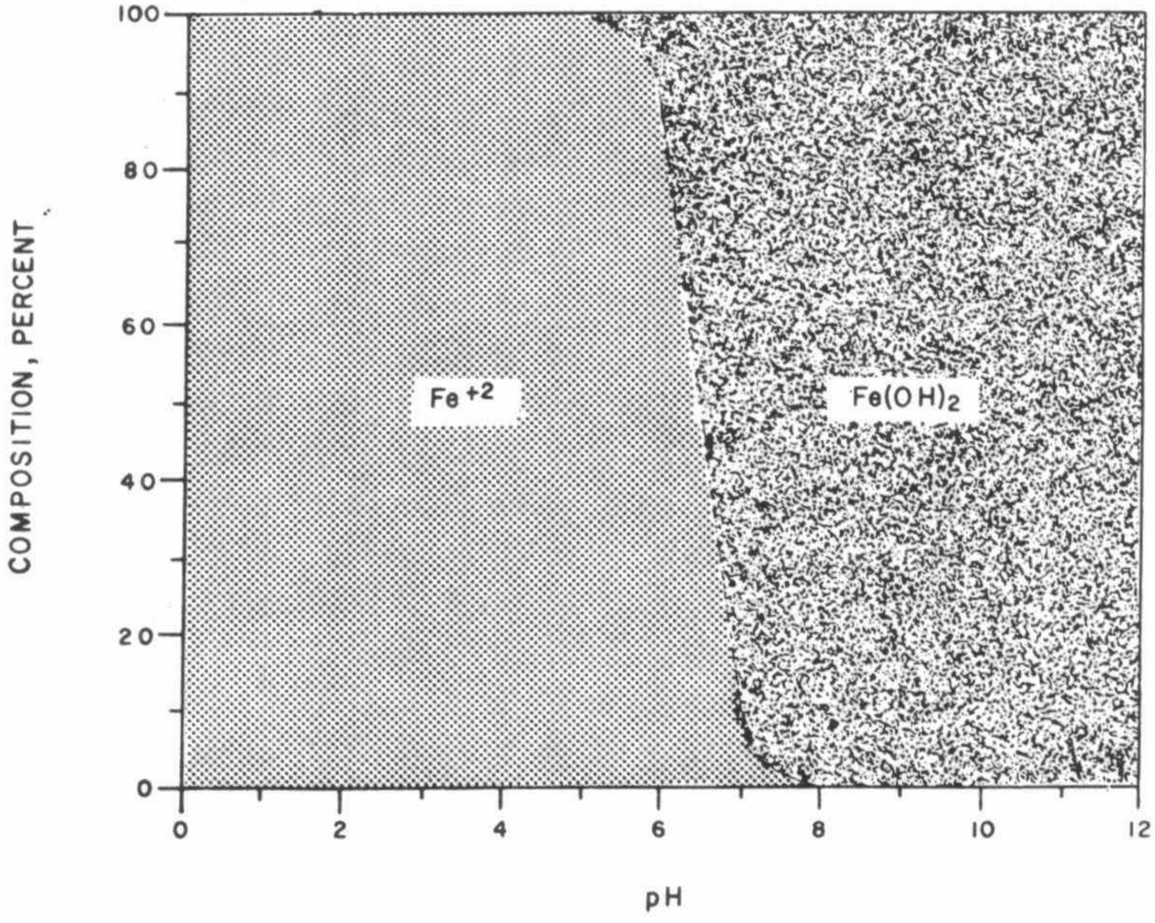

Table 1

EQUILIBRIUM COMPOSITION FOR THE SYSTEM Fe^{+2} - $Fe(OH)_2$ AT VARIOUS pH VALUES, EXPRESSED AS FRACTION OF TOTAL Fe^{+2} PRESENT

		$[Fe(OH)_2]s$			
pH	Fe^{+2}	1	2	$[Fe(OH)_2]a$	$[FeOH^+]$
5.0	.999	.000005	.000005	$.020 \times 10^{-8}$	.000002
6.0	.903	.047	.047	.000002	.002
6.5	.485	.253	.255	.00002	.0068
7.0	.087	.454	.457	.00002	.0019
7.5	.0094	.493	.496	.00002	.0013
8.0	.00095	.496	.499	.00002	.0002
9.0	.00001	.498	.501	.00002	.00002

s = solid

1 = $FeOH^+ + OH^- \dashrightarrow Fe(OH)_2$

2 = $Fe^{+2} + 2OH \dashrightarrow Fe(OH)_2$

a = aqueous

From these data it appears that about 50 percent of the $Fe(OH)_2$ formed at any pH is due to the intermediate reaction $FeOH^+ + OH^-$ while the remaining 50 percent is formed directly from $Fe^{+2} + 2OH^-$.

Fe^{+3} is also found in mine water and as described earlier, is soluble only under special conditions. Like Fe^{+2}, the solubility can be determined from a consideration of the various equilibria involved. Figure 2 is a distribution diagram showing the percent composition versus pH.

FIGURE 2 DISTRIBUTION OF Fe^{+3} AND $Fe(OH)_3$ AS A FUNCTION OF pH

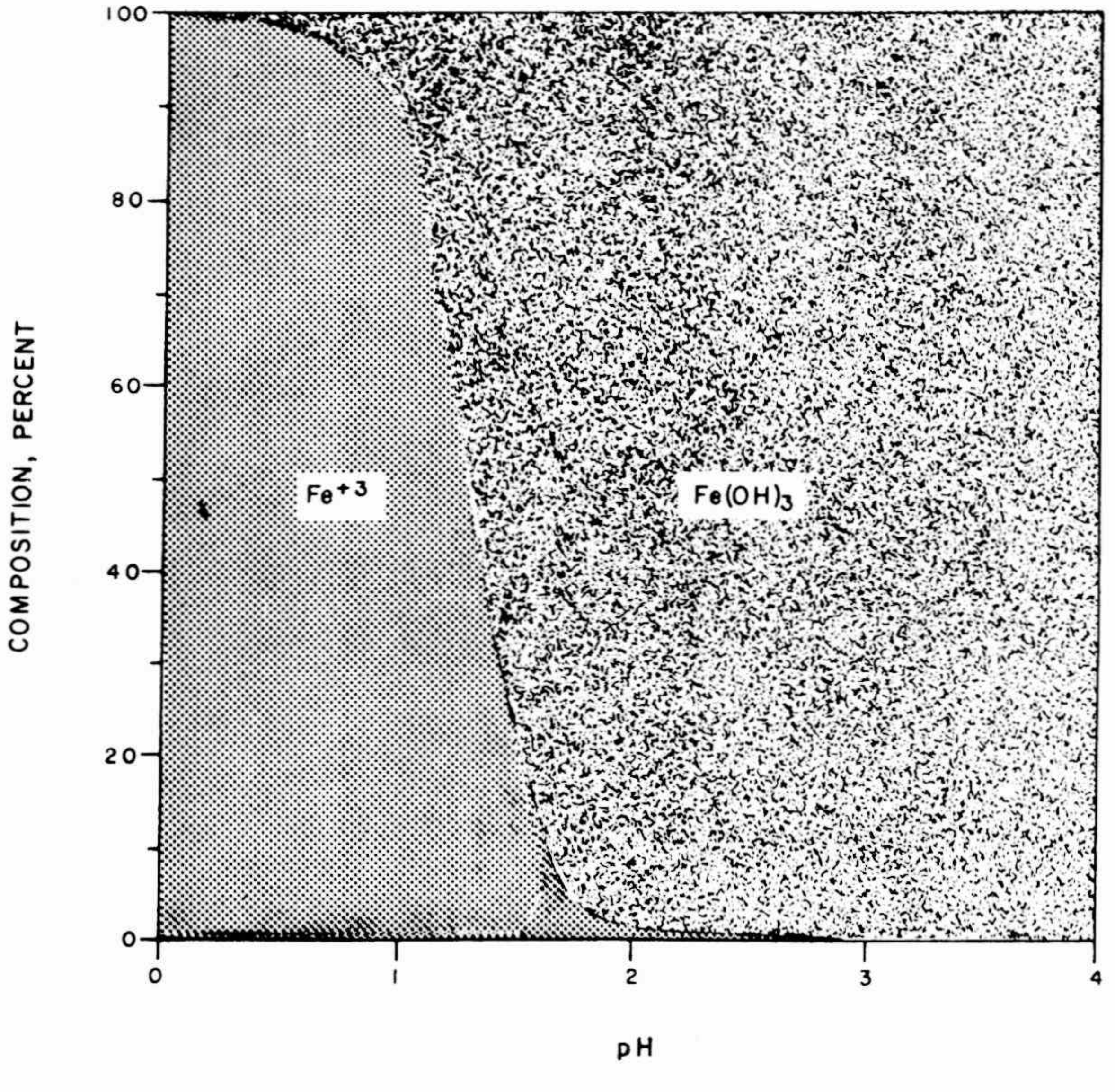

Table 2 gives the distribution at equilibrium of the various forms in which Fe^{+3} occurs at various pH levels.

Table 2

EQUILIBRIUM COMPOSITION FOR THE SYSTEM Fe^{+3} - $Fe(OH)_3$ AT VARIOUS pH VALUES, EXPRESSED AS FRACTION OF TOTAL Fe^{+3} PRESENT

pH	Fe^{+3}	$FeOH^{+2}$	$FeOH^{+2} + 2OH^- \rightarrow Fe(OH)_3$ a	$Fe^{+3} + 3OH^- \rightarrow Fe(OH)_3$ s
1.00	.8677	.0321	.0134	.0868
1.25	.1947	.4049	.0535	.3466
1.50	.0979	.1144	.4784	.3092
1.75	.0213	.0140	.5859	.3787
2.00	.0085	.0031	.1324	.8558
3.00	.000008	.00003	.1339	.8659

In addition to the above, $Fe(OH)^{+2}$ and $Fe(OH)_{3a}$ are also reported. The overall solubility of Fe^{+2} and Fe^{+3} in mine water is determined by many factors, none of which can be evaluated as an isolated variable; however, for both Fe^{+2} and Fe^{+3} the limiting solubility at any pH is the solubility satisfying the equations:

$$K_{sol}Fe(OH)_2 = [Fe^{+2}][OH^-]^2 \text{ and}$$
$$K_{sol_{Fe(OH)_3}} = [Fe^{+3}][OH^-]^3$$

as shown in Table 3.

Table 3

SOLUBILITY OF $Fe(OH)_2$ AND $Fe(OH)_3$ FROM K_{sol} AT 25 C

$K_{sol}Fe(OH)_2 = 5.25 \times 10^{-14}$;

$K_{sol}Fe(OH)_3 = 1 \times 10^{-38}$ (Also 10^{-40} is reported.)

pH	Fe^{+2}, ppm	Fe^{+3}, ppm
1		56000
2		560
3		0.56
4		0.00056
5		
6	29400	
7	294	
8	2.94	
9	0.0294	

General Equilibria for Ferrous Hydroxide

The dissolution of ferrous hydroxide in basic solutions can be attributed to one or more of the following reactions represented by the equations and formulas:

$$Fe(OH)_2\ (s) \rightleftharpoons Fe^{++} + 2OH^-$$

$$Fe(OH)_2\ (s) \rightleftharpoons FeOH^+ + OH^-$$

$$Fe(OH)_2\ (s) \rightleftharpoons Fe(OH)_2\ aq.$$

$$Fe(OH)_2\ (s) + OH^- \rightleftharpoons HFeO_2^- + H_2O$$

$$Fe(OH)_2\ (s) + 2OH^- \rightleftharpoons Fe_2O^= + H_2O$$

$$Fe(OH)_2\ (s) \rightleftharpoons HFeO_2^- + H^+$$

General Equilibria for Ferric Hydroxide

The dissolution of ferric hydroxide in neutral, acidic or basic solution can be attributed to one or more of the reactions represented by the equations:

$$FeOOH_{(s)} + H_2O \rightleftharpoons Fe(OH)_2^{+} + OH^{-}$$

$$FeOOH_{(s)} + 2H_2O \rightleftharpoons FeOH^{++} + 2OH^{-}$$

$$FeOOH_{(s)} + 3H_2O \rightleftharpoons Fe^{+++} + 3OH^{-}$$

$$FeOOH_{(s)} + OH^{-} \rightleftharpoons FeO_2^{-} + H_2O$$

$$FeOOH_{(s)} + 2OH^{-} \rightleftharpoons HFeO_3^{=} + H_2O$$

$$FeOOH_{(s)} + 3OH^{-} \rightleftharpoons FeO_3^{\equiv} + 2H_2O$$

$$FeOOH_{(s)} + H_2O \rightleftharpoons Fe(OH)_3\ aq.$$

$$FeOOH_{(s)} + H^{+} \rightleftharpoons FeO^{+} + H_2O$$

$$FeOOH_{(s)} + 2H^{+} \rightleftharpoons FeOH^{++} + H_2O$$

$$FeOOH_{(s)} + 3H^{+} \rightleftharpoons Fe^{+++} + 2H_2O$$

Evidence for designating ferric hydroxide by the formula given comes from Wells. (18)

As a base, ferric hydroxide is, as we should expect, much weaker than ferrous and accordingly the salts are much more highly hydrolyzed; the solutions, unless they are strongly acid, contain the ions $Fe(OH)^{++}$ and $Fe(OH)_2^{+}$, and as soon as the concentration of $Fe(OH)_3$ exceeds 0.00022 mg. per litre it begins to separate out in colloidal form. It

(18) A. F. Wells, "Structural Inorganic Chemistry" First Edition, Oxford Press, New York, N.Y., 1947, pp. 62, 350 and 365.

has a much stronger tendency to form complexes.

Oxidation of Ferrous Iron

The following is the verbatim synopsis of a report entitled "Oxygenation of Ferrous Iron" by Harvard University, Cambridge, Massachusetts, for the Federal Water Quality Administration--Department of the Interior, U.S.A., Contract PH 36-66-107, June, 1970:

> "The rate of oxidation of iron (II) by oxygen conforms to a relationship which is first-order in the concentrations of ferrous iron and oxygen, and second-order in the concentration of hydroxide ion, at pH-values between 6.0 and 7.5. The reaction proceeds relatively rapidly at pH-values greater than 6.5; the half-time of the reaction is 4 minutes at pH 7.0, under a partial pressure of oxygen of 0.20 atmospheres at 25°C. Deferrization processes in water treatment employ the rapidity of the oxidation reaction in order to remove the influent iron (II) as insoluble iron (III) hydroxide. Part of the iron (II) may also be removed as ferrous carbonate ($FeCO_3$), the solubility product of which is 6.0×10^{-11}, as shown by this research.
>
> The dependence of the oxidation rate on $[OH^-]$ has been observed, in this study, at pH-values as low as 4.5, where the half-time has increased to approximately 300 days. At lower pH-values, the dependence of the reaction rate on pH (or, more precisely, $[OH^-]$) becomes less marked until at pH-values below 3.5, the oxidation proceeds at a rate which is independent of pH. Here, a half-time of about 2000 days reflects the slowness of the oxidation reaction.
>
> In the acidic drainage waters issuing from coal mines, half of the acidity arises from the oxidation of the sulfide (S_2(-II)) of iron pyrite (FeS_2) to sulfate, and half stems from the oxidation of iron (II) to iron (III) by oxygen and the subsequent hydrolysis of the resultant iron (III). Observations of the rate of oxidation of ferrous to ferric iron in these acidic streams (at pH values close to 3) show it to proceed considerably more rapidly than the laboratory studies at pH 3 would predict.
>
> Several chemical agents which are indigenous to mine drainage waters have been cited in the literature, in

various circumstances, as displaying catalytic properties in the oxidation of ferrous iron. These include inorganic ligands, such as sulfate, which coordinate with iron (II) and iron (III), soluble metal ions, such as copper (II), manganese (II), and aluminum (III), suspended material with large surface areas and high adsorptive capacities, such as clay particles, and materials which accelerate the decomposition of peroxides in the presence of iron (II), such as charcoal. An investigation into the catalytic capabilities of these chemical agents in synthetic mine waters demonstrates that clay particles, or their idealized counterparts alumina (Al_2O_3) and silica (SiO_2), exert the greatest influence on the rate of oxidation of iron (II), but only at areal concentrations much larger than those encountered in most natural mine waters. (The reaction proceeds 10-30 times more rapidly in the presence of $8000 m^2/l$ of Al_2O_3 than the uncatalyzed reaction.)

Autotrophic microorganisms have frequently been implicated as the causative agents in the production of acidic mine drainage. These organisms are able to utilize the energy released by the oxidation of ferrous iron for their metabolic processes. A study of the oxidation of iron (II) in natural mine streams near Elkins, West Virginia shows the reaction to proceed at a rate which is zero-order in iron (II). The field results suggest that the observed rapidity of the reaction in acidic mine waters is apparently the result of microbial catalysis.

Studies of the oxidation of iron pyrite in coal mine drainage have usually considered only oxygen as the specific oxidant, with the potentiality of iron (III) as an oxidant having often been overlooked. Experimental evidence obtained in laboratory systems shows that iron (III) is rapidly reduced by iron pyrite both in the presence and absence of oxygen. There is virtually no difference between the rate of reduction of iron (III) by pyrite, or the rate of change of soluble iron (II), under aerobic or anaerobic conditions indicating that the specific oxidant of iron pyrite is ferric iron.

The time required for the reduction of 50% of the initial iron (III) concentration in contact with 1 gram/liter of pyrite is approximately 250 minutes which is considerably less than the half-time for the oxidation of iron (II) even when accelerated by the chemical catalysts found in natural mine waters. Consequently, the rate-limiting step among the reactions involved in the oxidation of iron pyrite and the production of acidity in mine drainage waters is the oxygenation of ferrous iron.

Based upon the experimental evidence presented, the oxidation of iron pyrite in natural mine waters is shown to be compatible with a cyclical reaction model involving the slow oxygenation of iron (II) to iron (III) followed immediately by the rapid reduction of iron (III) by pyrite, generating in turn more iron (II) and acidity:

$$Fe(II) + O_2 \xrightarrow{slow} Fe(III)$$

$$Fe(III) + FeS_2 \xrightarrow{fast} Fe(II) + SO_4^{-2}$$

The oxidation of iron (II) by oxygen is the rate-determining reaction. Oxygen is involved only indirectly in the oxidation of pyrite; it serves to regenerate iron (III) which is itself the specific oxidant of pyrite. Precipitated iron (III) hydroxide within the mine serves as a reservoir for soluble iron (III)."

Quoting: An Experimental Investigation of the Treatment of Acid Mine Water Containing High Concentrations of Ferrous Iron with Limestone" by C. T. Holland, R. C. Berkshire, D. F. Golden, West Virginia University, Morgantown, W. Va.

"The slow reaction in the treatment of ferrous iron with calcium carbonate is explained by a study of the chemistry of the process.

When iron sulfate salts are dissolved in a water medium the compounds undergo hydrolysis reactions to liberate the hydrogen ion. Hydrolysis is defined as a reaction of an ion with water to form an associated species plus H_+ or OH^-. The general equation for a cationic hydrolysis is $M^+ + H_2O \leftarrow MOH + H^+$ so that in the case of iron salts the reactions would be for ferrous iron

$Fe^{+2} + H_2O \rightleftarrows FeOH^+ + H^+$ and

$FeOH^+ + H_2O \rightleftarrows Fe(OH)_2 + H^+$

and the net reaction would be $Fe^{++} + 2H_2O \rightleftarrows Fe(OH)_2 + 2H^+$ and for ferric iron $Fe^{+3} + H_2O \rightleftarrows Fe(OH)^{+2} + H^+$

$$\mathrm{Fe(OH)^{+2} + H_2O \rightleftharpoons Fe(OH)_2^{+} + H^{+}}$$

$$\mathrm{Fe(OH)^{+2} + H_2O \rightleftharpoons Fe(OH)_3 + H^{+}}$$

the net reaction being

$$\mathrm{Fe^{+3} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^{+}}$$

These are equilibrium reactions and will go to completion (i.e., completely hydrolyzed) only if the hydrogen ion is pulled out of the equilibrium. This can be accomplished by neutralizing the proton with a base.

Calcium carbonate in an acidic medium will undergo a reaction to form lime and carbon dioxide according to the equation:

$$\mathrm{CaCO_3 + H_2O \rightleftharpoons CaO + H_2CO_3}$$

where $\mathrm{H_2CO_3 \rightleftharpoons H_2O + CO_2}$

The lime will react with the acid proton to neutralize it and form water plus the calcium salt of the protonic acid:

$$\mathrm{CaO + 2H^{+} \longrightarrow Ca^{++} + H_2O}$$

For the case of ferric sulfate. The reactions would be $\mathrm{Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4}$ and $\mathrm{3CaO + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O}$. The reaction of calcium carbonate with an acid to form lime will occur just above pH 7 and the precipitation of ferric hydroxide occurs around pH 5.5. Therefore as $\mathrm{CaCO_3}$ is added to the acidic $\mathrm{Fe_2(SO_4)_3}$ solution lime is liberated to neutralize the acid formed by hydrolysis and to precipitate the ferric hydroxide. Ferrous hydroxide will not precipitate from the water solution until a pH = 9.5-10 is reached. Since the natural pH of calcium carbonate solutions is around pH = 8 and since carbon dioxide must be liberated from $\mathrm{CaCO_3}$ in acid to produce lime, it is not surprising that as any free acid generated by the partial hydrolysis of ferrous iron is used by $\mathrm{CaCO_3}$ to form lime the pH rises above pH-7, stops the reaction of $\mathrm{CaCO_3}$ to form lime as well as the complete hydrolysis of the ferrous salt to form hydrogen ions and eliminates the possibility of precipitating ferrous hydroxide from the solution. If lime instead of $\mathrm{CaCO_3}$ is used then the pH will rise to around pH-10 and all of the ferrous iron should be precipitated.

It is obvious from the study of the above chemistry, that if water containing large quantities of ferrous iron is to be purified by treatment with calcium carbonate, that more will have to be done than simply introducing the calcium carbonate into the water. The experimental work described above indicates that the ferric iron will be reacted with rapidity and also indicates that the ferric iron will be precipitated readily. The above chemistry also indicates that the ferrous iron must be oxidized to ferric iron with the formation of free acid before the calcium carbonate can react with it. This may be done by vigorously aerating the solution containing the ferrous iron and the calcium carbonate for a fairly long period."

Oxidation of Ferrous Iron - Catalytic Effects Due to Impurities

From "Oxygenation of Ferrous Iron" by Stumm and Lee, Harvard University, 1961.

"Cupric ion is an efficient catalyst in many oxidation reactions. Even trace quantities of Cu^{+2} have a pronounced effect on the oxidation rate of ferrous iron in acid solutions. The catalytic effect is considerable for $Cu^{+2} = 3 \times 10^{-7}$ M, but increases only slowly with increasing Cu^{+2}".

NOTE: The above is in qualitative agreement with the work of Cher and Davidson (J. Am. Chem. Soc., 77, 793) (1955).

"The results of the above authors have been accounted for by the following mechanism:

$$Fe^{+2} + Cu^{+2} \rightleftharpoons Fe^{+3} + Cu^{+} \quad (a)$$

$$Cu^{+} + O_2 \rightleftharpoons Cu^{+2} + HO_2 \quad (b)$$

The HO_2 is assumed to react further with Fe^{+2} as in the Weiss mechanism; i.e.,

$$Fe^{+2} + O_2 \rightleftharpoons Fe^{+3} + HO_2 \quad (a)$$

$$Fe^{+2} + HO_2 \longrightarrow Fe^{+3} + H_2O_2 \quad (b)$$

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + HO + H_2O \quad (c)$$

$$Fe^{+2} + HO \longrightarrow Fe^{+3} + H_2O \quad (d)"$$

Reference for above: Weiss, J., Naturwissenschaften, 23, 1935.

"The data obtained do not permit the formulation of a meaningful rate expression which would account satisfactorily for the catalytic effect of copper. However, several qualitative statements can be made. The same proportionate acceleration of the oxygenation rate was observed at any pH value within the pH range investigated. The runs made in the presence of Cu^{+2} show the same temperature dependence as those made in the absence of Cu^{+2}. The catalytic effect of Cu^{+2} is dependent upon both the initial ferrous and ferric iron concentrations. Higher initial ferrous iron concentrations and/or an incipient addition of ferric iron causes an increased rate of reaction. There is a saturation concentration of Cu^{+2} for any given initial ferrous iron above which further addition of Cu^{+2} has little or no effect on the reaction rate. The addition of various amounts of complex formers such as glycine, tetramine, and ethylene diamine tetraacetate did not affect the reaction rates. The latter two complexing agents markedly retard the oxygenation reaction in the absence of Cu^{+2}. Copper complexes appear to be as effective catalysts as the aqueous copper ions."

Evidence exists that other metal ions (Mn^{+2}, Co^{+2}) as well as anions (besides OH^-) which form complexes with Fe^{+3}, $H_2PO_4^-$, metaphosphate are capable of hastening the oxygenation reaction.

Aspects of Ferric (Iron) Chemistry

Ferric iron plays an extremely important role in the formation of acid mine drainage. It is one of the agents that is responsible for the decomposition of the iron sulphides and of many of the 'ore' sulphides.

The following is taken from "Sulphide to Sulphate Reaction Studies" by Smith, Svanks and Shumate, Ohio State University, Columbus, Ohio (Research Grant WP-00340).

"Ferric ions have been reported by several authors to be an important agent in pyrite oxidation. Garrels and Thompson performed an interesting series of experiments in which pyrite from three different localities was oxidized by ferric sulfate solutions. They followed the change in ferric/ferrous concentration ratio by measuring the oxidation-reduction potential (E_h) of solution. Due to the rapid oxidation at high ferric ion concentration (high E_h) and rapid change in E_h in the initial phases of their experimental runs, they were not able to obtain oxidation rates at ferric-to-total iron concentrations of over 99.9%. As will be shown later, it is important in interpreting mechanism to know oxidation rates at (essentially) 100% ferric ions. For this reason, equipment was developed to measure oxidation rate at any selected value of EMF* (or E_h). Here again, the oxidation rate, expressed in microgram-moles pyrite oxidized per hour per gram pyrite is based on a stoichiometry of 14 moles of ferric ions reduced per mole of pyrite oxidized (to the sulfate). This stoichiometry, reported by Garrels and Thompson, was verified for samples which had been "conditioned" by prior oxidation. In those cases where freshly-prepared pyrite was used, the stoichiometric ratio started at values that more closely corresponded to oxidation of the sulfide to elemental sulfur rather than the sulfate; i.e., two moles of ferric ion reduced per mole of pyrite oxidized. But after 24 to 48 hours reaction time, the former stoichiometry held.

One conclusion that may be drawn from the data is that the redox potential (E_h) by itself, is not a measure of the anaerobic oxidation rate. The particular ionic reaction responsible for the E_h is the real variable. Ferric ion concentration and the ferric/ferrous ratio, which is indicated by E_h, determine reaction rate.

Because these anaerobic studies indicate ferric ions are the oxidizing agent for pyrite, and since the rates for both aerobic and anaerobic oxidation are similar, it is very possible that the ultimate oxidizing agent for both anaerobic and aerobic oxidations is ferric ions.

If ferric ions are assumed to be the oxidizing media in aerobic oxidations, then the rate of oxidation of ferrous to ferric ions must be equivalent, at steady state, to the rate of pyrite oxidation. Rate of oxidation of ferrous to ferric, in solution, has been investigated by Huffman and Davidson, and Stumm and Lee at low pH's and in natural waters. The rate of ferrous oxidation in solutions is many orders of magnitude less, under any condition, than that which must exist to account for pyrite oxidation. However, it is possible that pyrite surfaces act as a catalyst to greatly increase the rate of oxidation of adsorbed ferrous ions.

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* E_h = EMF + (EMF) Ref. Cell = EMF + 0.242

Several other observations support the view that aerobic reaction rate is independent of the ferrous ion oxidation in solution. First, the rate of aerobic pyrite oxidation is independent of iron concentration. Second, the rate is not determined by the ferric/ferrous ratio in solution. For example, the ferric/ferrous ratio in liquid phase oxidation at pH = 2, and a partial pressure of oxygen of 76 cm. Hg. is approximately 0.08. The oxidation rate under these conditions is 2.1 micrograms pyrite oxidized per hour per gram sample. For ferric ion oxidation the rate at the same ferrous/ferric ratio is less than 0.14.

Evidently there is some difference in the nature of the "reactive site" involved in anaerobic and aerobic oxidation.

However, the "reactive site" for aerobic oxidation may be an adsorbed ferrous ion (possibly a chemisorbed ion), which is catalytically oxidized to ferric. It in turn accepts an electron from the pyrite and is reduced to its original state, thus regenerating the reactive site. In such a situation the rate would be independent of the iron concentration in solution.

Microbial Oxidation:

The large increase in anaerobic reaction rate as the ferric-to-ferrous ratio approaches infinity could account for the increase in rates due to microbial activity. Dugan and Lundgren report the energy supply for Ferrobacillus ferrooxidans to be oxidation of ferrous to ferric ions. The rate of oxidation at relatively low pH is greatly accelerated by the presence of these bacteria. At pH below 4, the concentration of ferric ions could be high enough to have a significant effect on rate.

Konecik used massive concentrations of Ferrobacillus ferrooxidans to determine the maximum oxidation rate that could be achieved in a microbial-catalyzed system. For a particular type and weight of pyrite, he found a quantity of bacteria above which the rate of reaction did not increase. It is possible that at this "optimum" concentration of bacteria, the rate of oxidation of ferrous to ferric is sufficiently high to maintain essentially 100% ferric ions. Since the pH was below 2.5, the concentration of iron was high enough that oxidation rate would be independent of concentration.

pH Effects:

In developing the rate equations for both aerobic and anaerobic oxidation, the tacit assumption was made that the only substances competing for the "reactive sites" were oxygen and dissolved inerts for the aerobic, and ferrous and ferric ions for the anaerobic reaction.

Actually, the adsorption occurs from an aqueous solution so that water itself is competing for reactive sites. Even more important, the nature of the adsorption as well as the number of "reactive sites" might well depend on the relative concentration of OH^- and H^+ (pH) of the aqueous solution. It has been shown that metal oxides and many natural minerals exhibit ion exchange capacity arising from a pH dependent surface charge. The oxides are cation exchangers in a basic environment when the surface charge is negative, and anion exchangers in acid environment. Adsorption is reported to be due to many other factors than surface charge, but the extent of adsorption decreases rapidly when the sign of the surface charge changes to that of the adsorbed material.

Assuming the disulfides' surface charge is similar or varies in the same direction as the oxides', adsorption of ferrous and ferric ions would increase rapidly as the environment is made more basic, i.e., as the surface charge becomes more negative. There are undoubtedly forces (e.g., coordinate bonding) other than electrostatic involved in this adsorption, but these too would be influenced by the pH of the solution, resulting in a change in reaction rate with pH.

Based on present knowledge, a possible mechanism involved in the sulfide-to-sulfate reaction may be described as follows:

The final electron transfer is through the reduction of a ferric ion specie adsorbed on a "reactive site" of pyrite.

The ferric specie may be adsorbed as a ferric ion from a solution of high E_h or as a ferrous ion; the adsorbed ferrous ion is then catalytically oxidized to ferric by oxygen adsorbed on the active site formed by the ferrous ion.

Under the laboratory conditions used, the rate-limiting step is the surface, electron transfer, reaction.

In oxidation by ferric ions, rates are determined by concentration and ferric/ferrous ratio. Since adsorption of ferrous ions is much greater than ferric, rates increase rapidly as the ferric/ferrous ratio approaches infinity.

Aerobic oxidation rates are much higher than the corresponding anaerobic rate at the same ferric/ferrous ratio, and orders of magnitude higher than can be accounted for by chemical oxidation of ferrous ions in solution, thus leading to the conclusion that solution reactions are insignificant in a purely chemical system. It is possible that the ferric/ferrous ratio can be increased by microbial action to the point that the ferric/ferrous ratio is rate-determining in an aerobic system. The possibility increases as the oxygen concentration decreases."

The following 'conclusions' were taken from "Sulphide to Sulphate Reaction Mechanism" by Ohio State University Research Foundation, Grant No. 14010FPS, February 1970. The conclusions are relevant to ferric chemistry:

"The following major conclusions may be drawn from information obtained during the course of this project:

(1) The principal mineralogical form of naturally occurring iron disulfide materials in Eastern coal mining areas is pyrite.

(2) The major factor influencing reactivity of various types of pyritic material is surface area (texture), not trace elements or included minerals.

(3) The rate-determining reaction in "natural" systems, in the absence of mass transport limitations, is an electron transfer between the oxidizing agent (oxygen or ferric ion) absorbed on the surface of pyrite, and the pyrite itself.

(4) There are two modes of pyrite oxidation as determined by the immediate oxidizing agent; i.e., oxygen or ferric ions. Each oxidation mode is independent of the other. For a given pyrite surface, oxygenation rate is, for all practical purposes, dependent only on the oxygen concentration in the aqueous phase surrounding the reactive site on the pyrite surface and independent of other solute concentration. Ferric ion oxidation is primarily determined by the ferric/ferrous ratio and free ferric ion concentration, and is not affected by dissolved oxygen.

(5) Kinetics for the oxygenation of pyrite have been experimentally determined as a function of (a) temperature, (b) oxygen concentration, (c) pH, (d) water partial pressure, (e) surface area (or texture), and (f) concentration of iron, sulfate, and other ions.

(6) Kinetics of pyrite oxidation by ferric ions have been determined as a function of (a) ferric/ferrous ratio, (b) total iron concentration, and (c) free ferric ion and hydrogen ion concentration (qualitatively).

(7) Ferric ion oxidation of pyrite is the chemical analogy of microbial-enhanced pyrite oxidation.

(8) Significant microbial catalysis will occur only if the water-to-pyrite ratio is sufficiently high to provide for the required population of organisms."

Similarly, the following "Summary and Conclusions" was taken from "Some Factors Influencing the Biological and Non-Biological Oxidation of Sulphide Minerals" by Bryner, Walker and Palmer, Brigham Young University, 1967:

"The purpose of this investigation was to further study some of the factors affecting the air oxidation of sulfide minerals such as temperature, soluble iron; hydrogen ion concentrations and catalysts.

The effect of temperature on the biological oxidation of pyrite and copper (II) sulfide was studied over the range from 25°C to 75°C. The optimum biological oxidation for pyrite was near 35°C and dropped off to a minimum near 65°C with a slight increase at 75°C. The optimum for the biological oxidation of copper (II) sulfide was 35°C and a minimum at 55°C; the non-biological oxidation increased with the temperature for the copper (II) sulfide.

Iron (III) is known to be effective in the oxidation of many sulfide minerals. Since it is known that activated carbon is a catalyst in the air oxidation of iron (II), it was used to increase the oxidation of iron (II) in the presence of the mineral. Studies were also made on the biological oxidation of sulfide minerals and compared to the non-biological oxidation.

The effect of activated carbon was marked on the copper (II) sulfide and chalcopyrite. This indicates that activated carbon has a surface action effect on the oxidation of the mineral in addition to its effect on the oxidation of iron (II). This catalytic action is direct oxidation of the mineral by absorbed oxygen from the air or catalysis of the oxidation of the mineral by iron (III).

In the oxidation of copper (II) sulfide the bacteria have an optimum iron (II) concentration of about 0.5 gm/litre. Studies with carbon also indicate that only a small amount of iron (II) is needed for efficient oxidation of copper (II) sulfide.

The oxidation of cuprite and copper was studied to determine the effect of iron (II) and (III) on the air oxidation of copper. Iron (II) or (III) act as intermediate catalysts in the air oxidation of copper in dilute sulfuric acid solution. Activated carbon and iron (II) increased the rate of oxidation of free copper.

The air oxidation of pyrite in 0.1 N sulfuric acid, with iron (II) and activated carbon or iron (III) was 15 times faster than when the iron salts were absent. Iron (III) oxidized about 1/3 as much pyrite in the absence of air as it did in the air.

In the biological oxidation of sulfide minerals, the bacteria catalyze the oxidation of iron (II) to (III), which in turn acts as a catalyst in the oxidation."

And from "Oxidation of Pyrite by Iron Sulphate Solutions" by Garrels and Thompson, Harvard University, Am. Journ. Sc., Bradley Volume, Vol. 258-A, 1960:

"Oxidation of pyrite specimens by ferric sulfate solutions shows that pyrites from different localities oxidize at markedly different rates, but apparently the mechanism is the same. The rate of oxidation is chiefly a function of the oxidation potential of the solution, and is independent of the total iron content.

The oxidation process, over the range of ferric ion concentration from 100% to less than 0.1 percent $m_{Fe^{+++}}$, apparently is controlled by differential adsorption of ferric and ferrous ions on the pyrite surface. All our data are explained if it is assumed that the rate of oxidation is proportional to the fraction of pyrite surface occupied by ferric ion, and if the occupation of pyrite surface by ferric and ferrous ions is approximately proportional to their concentrations in solution. Thus if pyrite is placed in a solution containing ferric and ferrous ions, rapid adsorption of both species apparently takes place on the pyrite surface. Reaction to ferrous ions and sulfate ions occurs only at those sites occupied by ferric ions. Because the oxidation process is slow relative to adsorption, the adsorption process controls the rate.

Impurities in solution such as nickel, cobalt, vanadium, manganese, copper, and cerium have little effect on oxidation rate, with just a hint that vanadium accelerates oxidation and copper retards it. The oxidation rate is independent of pH in the range 0 to 2. (No ferric hydroxides are formed.)

Except under near-equilibrium conditions, pyrite is apparently oxidized by ferric ion to ferrous ion, hydrogen ion, and sulfate ion. The first step of the oxidation process, however, may be to produce molecular sulfur.

Because of the exponential increase in oxidation rate as the ratio of ferric ion to total iron increases, pyrite changes from an essentially inert substance at Eh values in the vicinity of 0.300-0.400 volts, to an active reducing agent at potentials of 0.800 volts and above."

The Hydrolysis of Ferric Iron in Sulphate Solution

When ferric sulphate hydrolyses, a precipitate is generally formed. The precipitate may be in the form of either a hydrated ferric oxide or a basic sulphate. If in the form of a basic sulphate, a degree of sulphate removal may be achieved.

From "The Hydrolysis of Ferric Iron in Sulphate Solution" by T. V. Arden, Chemical Research Laboratory, Teddington, Middlesex, England (1950):

"Ferric sulphate hydrolyses in three stages, to $FeOH^{++}$, $Fe(OH)_2^{+}$, and a precipitate whose composition varies according to the dilution. The reaction constants for the formation of $FeOH^{++}$ and $Fe(OH)_2^{+}$ have been found from pH measurements to be $K_1 = 1.25 \times 10^{-3}$ $K_2 = 4.2 \times 10^{-4}$ at 25°. There is evidence for the presence in solution of an acid complex, which may be ferrisulphuric acid, $(FeOH)(HSO_4)_2$.

The immediate reaction of sodium hydroxide with ferric sulphate solution gives an unstable solution containing high concentrations of the basic ions. When the ratio NaOH:Fe exceeds 0.5:1, a precipitate of $2Fe_2O_3.SO_3$ is formed, precipitation being complete when the ratio is 2.5:1. The addition of more sodium hydroxide causes the conversion of this precipitate into ferric hydroxide. On storage, solutions having a ratio of less than 0.5:1 deposit ferric oxypentasulphate [ferric (2:5) sulphate], $2Fe_2O_3.5SO_3$, which is stable for long periods. The precipitate of $2Fe_2O_3.SO_3$ [ferric (2:1) sulphate] is slowly dehydrated, and then hydrolyses further during several months to give ferric octaoxysulphate [(3:1) sulphate], $3Fe_2O_3.SO_3$.

The ferric hydroxide precipitate is stable for an indefinite period at less than pH 7.0. In the presence of excess of sodium hydroxide, it is slowly dehydrated to form goethite, $2Fe_2O_3.H_2O$."

"The Basic Sulphates.--The evidence of this work indicates the formation, according to the conditions, of three basic sulphates: ferric oxypentasulphate, $2Fe_2O_3.5SO_3.xH_2O$, corresponding to the mineral copiapite; ferric pentaoxysulphate, $2Fe_2O_3.SO_3.xH_2O$, equivalent to the minerals glockerite and hydroglockerite; and ferric octaoxysulphate, $3Fe_2O_3.SO_3.xH_2O$, which has not previously been reported. The postulation of the ions $FeOH^{++}$ and $Fe(OH)_2^{+}$ suggests that the corresponding basic sulphates $2Fe_2O_3.SO_3$ and $Fe_2O_3.SO_3$ may occur as intermediate stages in the hydrolysis and titration processes. It is known that ferric oxydisulphate, $Fe_2O_3.2SO_3$, occurs as a series of minerals in various states of hydration between those of butlerite ($2H_2O$) and fibroferrite ($10H_2O$). Similarly, ferric dioxysulphate [(1:1) sulphate], $Fe_2O_3SO_3$, exists as borgstromite (anhydrous) and planoferrite ($15H_2O$), together with intermediate compounds. Posnjak and Merwin (J. Amer. Chem. Soc., 1922, 44, 1983), in phase-rule studies at 75-200°, showed that $Fe_2O_3.2SO_3$ occurred as a solid phase at all temperatures, the hydration varying according to the temperature. The results of this work do not indicate the presence of either ferric dioxysulphate or ferric oxydisulphate for any finite period of time at 25°. One observation exists, however, to suggest their momentary formation during the initial equilibrium stage. It has been shown that in the intermediate equilibrium stage, ferric pentaoxysulphate occurs in three forms which can be distinguished visually, the boundaries between them coinciding with inflexions in pH. Since the state of the solution at the intermediate stage is little changed throughout the titration, the difference in the form of the precipitate must result from some difference in the mechanism of precipitation. A possible process would be the initial formation of $Fe(OH)SO_4$, $[Fe(OH)_2]_2SO_4$, and $[Fe_2(OH)_5]_2SO_4$ in these regions, followed immediately by their conversion into three forms of $[Fe_2(OH)_5]_2SO_4$, which lose water during the second equilibrium stage, to give three different hydrates of $2Fe_2O_3.SO_3$.

Basic Ions.--The hydrolysis of ferric sulphate solutions can be explained quantitatively by the postulation of the ions Fe^{+++}, $FeOH^{++}$, and $Fe(OH)_2^{+}$ as the only ones present in solution. The presence of FeO^{+} ions in solutions obtained from the ultra-filtration of ferric hydroxide sols has been demonstrated by Krestinskaya and Khavimov (J. Gen. Che. U.S.S.R., 1944, 14, 70), and evidence for the existence of $FeOH^{++}$ has been given by the absorption-spectra studies of Rabinowitch and Stockmeyer. The formation of ferric oxypentasulphate and ferric pentaoxysulphate, which can be considered as the sulphates of Fe_2OH^{5+} and $Fe_2(OH)_5{}^+$, suggests the possibility that the hydrolysis process may occur through the medium of diatomic ions. In this case, equilibria would occur between Fe^{3+}, $Fe_2{}^{6+}$, Fe_2OH^{5+}, $Fe_2(OH)_2{}^{4+}$, $Fe_2(OH)_4{}^{2+}$, and $Fe_2(OH)_5{}^+$. No evidence has been found for an ion of the type $Fe_2(OH)_3{}^{3+}$."

Other references used in this Section:

> "Tailings Disposal, Generation of Acidity from Pyrrhotite and Limestone Neutralization of Wastewater at Falconbridge's Onaping Mines" by Rivett and Oko, The Canadian Mining and Metallurgical Bulletin, August 1971.
>
> "Status of Mine Drainage Technology" by E. A. Zawadzki, 1967, Bituminous Coal Research, Inc., 350 Hochberg Road, Monroeville, Pennsylvania.

THE CHEMISTRY OF ACID MINE DRAINAGE

PART B - MICROBIOLOGICAL ASPECTS OF ACID MINE DRAINAGE

A topic that is frequently associated with the subject of acid mine drainage is microbiological leaching of sulphide minerals. Microbiological leaching involves the oxidation of the sulphide portion of various metallic sulphides with the subsequent release of the metal values into solution. Three names have been given to bacteria capable of oxidizing sulphide minerals:

(1) Thiobacillus ferrooxidans;

(2) Ferrobacillus ferrooxidans; and

(3) Thiobacillus sulfooxidans.

However, it has been shown that there is no justification for separating the bacteria into different genera and species and, as such, the name T. ferrooxidans has been suggested for the group.

Like many bacteria, T. ferrooxidans is ubiquitous, and its activities are manifested in leaching wherever a sulphide substrate, oxygen, carbon dioxide, water, certain essential nutrients and the correct pH make up a suitable environment.

T. ferrooxidans belongs to a somewhat select group of bacteria which are rather independent in temperament, and which probably existed on this earth long before those other microbial forms which are inter-dependent for many of their foods and conditions of life. In contrast to most bacteria, T. ferrooxidans uses atmospheric carbon dioxide as its sole source of the carbon necessary for the generation of cellular material. Rather than utilizing organic matter such as fats, carbohydrates or proteins as a source of energy, this organism cannot even tolerate their presence, and obtains its energy solely by the oxidation of inorganic materials such as ferrous iron or sulphur in the form of elemental sulphur or as metallic sulphides.

T. ferrooxidans has adapted itself to live and grow in the strongly acidic environment (pH 1.5 - 3.0) which results from the oxidation of sulphides, and in the presence of many heavy metals which are released into solution fromminerals concurrent with the oxidation of ferrous iron and sulphides. In order for T. ferrooxidans to function in the biological leaching of sulphides, the pH must be below 4 and preferably below 3. Apparently, the organism can oxidize sulphur at pH's as high as 5, but it will only occasionally oxidize sulphide at pH's above 3.5, and never above 4.0.

In attacking the sulphide moiety in crystalline or amorphous substances, the bacteria convert the sulphide to sulphate and, with the disruption of the solid matrix, the metal ions go into solution. These metals remain in solution as water-soluble sulphates initially, although iron may be subsequently precipitated as the insoluble hydroxide or basic sulphate. The hydrolysis of the ferric sulphate produces sulphuric acid along with either the ferric hydroxide or basic ferric sulphate. The sulphuric acid modifies the pH in the micro-environment immediately surrounding the bacteria. If there is no external disruption, the pH frequently tends to stabilize near pH 2 due to the resolubilization of ferric hydroxide. If there is excess pyrite or pyrrhotite present, it will go lower; pH values as low as 0.9 having been attained. pH values below 1.2 have a definite detrimental effect on the bacteria, interfering with their activity and resulting in the production of elongated cells.

Although T. ferrooxidans survives in conditions that are highly toxic to most other forms of life, it still must have oxygen to live. Every pound of sulphur (either as native sulphur or as sulphide) requires two pounds of oxygen for complete conversion to sulphate. Similarly, the bacteria require 0.14 pounds of oxygen for every pound of iron converted from the ferrous to the ferric form.

Phosphate and ammonia appear to be the most critical nutrients with regard to the nutrient requirement of T. ferrooxidans.

NOTE: From "Ferrobacillus Ferrooxidans: A Chemosynthetic Autotrophic Bacterium" by Leathen, Kinsel and Braley, Mellon Institute, Pittsburg, Pennsylvania, 1956.

"The ammonium ion....is the essential source of nitrogen. Nitrates do not appear necessary for growth."

Substrates Oxidized by Thiobacillus Ferrooxidans

Substrate	End Product
Ferrous Iron Fe^{++}	Fe^{+++}
Trithionate $S_3O_6^=$	$SO_4^=$
Tetrathionate S_4O_6	$SO_4^=$
Thiosulphate S_2O_3	$SO_4^=$
Sulphur S^o	$SO_4^=$
Sulphide $S^=$	$SO_4^=$

Metallic Sulphides Known to be Oxidized by Thiobacillus Ferrooxidans

Arsenopyrite	$Fe_2As_2S_2$
Bornite	Cu_5FeS_4
Bravoite	$(Ni, Fe)S_2$
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Cobaltite	CoAsS
Covellite	CuS
Enargite	$Cu_3(As, Sb)S_4$
Marcasite	FeS_2
Marmatite	(Zn, Fe)S
Millerite	NiS
Molybdenite	MoS_2
Orpiment	As_2S_3
Pyrite	FeS_2
Pyrrhotite	Fe_7S_8
Sphalerite	ZnS
Stannite	Cu_2FeSnS_4
Tetrahedrite	$Cu_8Sb_2S_7$
Violarite	$(Ni, Fe)_3S_4$

Temperature is another factor which can influence biological leaching. The optimum temperature for biological leaching has been found to be 35°C. The bacteria are inhibited at temperature of 40°C and above. When no other factors have become rate controlling, the rate of leaching decreases as the temperature decreases; as yet, however, no minimum temperature has been established. Leaching is known to occur slowly at 3°C to 6°C.

There is a serious problem in interpreting, for field use, the results obtained in fundamental biological investigations of acid mine drainage. There is no doubt, however, that the role of bacteria in acid mine drainage formation is significant.

From: "Microbial Factor in Acid Mine Drainage Formation" by Mellon Institute, Carnegie-Mellon University, Pittsburgh, Pennsylvania, FWQA Grant No. 14010 DKN,1970.

"The role of chemoautotrophic microorganisms (Ferrobacillus ferrooxidans, Ferrobacillus sulfooxidans, and Thiobacillus thiooxidans) in the formation of acid mine drainage from pyritic materials associated with coal mining has been studied using pilot plant reactors. The units were charged with crushed pyrite from actual mining sites. Most of the tests were conducted with horizontal, flooded-bed reactors through which water of fixed mineralization was passed at a controlled rate of flow.

Dissolution of pyrite, FeS_2 or iron sulfide, leads to ferrous (Fe II) ion and the sulfur species, S_2^{-II}. These are subsequently oxidized to ferric and sulfate reaction products. When the microorganisms were added to the system the unit is described as being seeded. Non-seeded is used to describe the condition when the organisms were not added.

The conclusions are:

(1) The concentration of acidity, ferrous ion and total iron and sulfate in effluents from pyritic beds is zero order with respect to flow if the flow is expressed in reciprocal time units, Day^{-1}, (total volume of water per day - volume of pyrite bed) over the range of 4.6 to 13.8, Days^{-1} or 1.5 to 4.3 hours retention time. At low flow rates of water flow the reaction products are mass transport limited and increase in concentration as flow decreases.

(2) There is continuous release of Fe (II) and S_2^{-II} from non-aerobic pyritic systems. The mass per unit time discharged is constant if the flow of water is not so low as to be diffusion rate limited. Pyrite dissolution takes place in the absence of air (oxygen) although at a lower rate than under aerobic conditions. Since the Fe (II) and S_2^{-II}-utilizing chemoautotrophic microorganisms are aerobes they are not active and do not affect release of these ions under nonaerobic conditions.

(3) Under aerobic conditions a mycelial growth may develop in the pyritic beds despite an acidic pH of 3 to 4.5. There was no evidence that the presence of the heterotrophic organisms affected chemoautotrophic organism activity or altered the mass of acid mine drainage released per unit time. Acid mine drainage discharge was similar in periods of high or low algal growth.

(4) The effect of flow rate on effluent characteristics was examined for nonaerobic, aerobic-nonseeded and aerobic-seeded operating conditions. Flow was varied to provide retention times through the pyritic beds of 1.5 to 10 hours.

a) The effluent pH under nonaerobic conditions increased slightly over feedwater pH of 4.5 because of dissolution of alkaline materials in the pyritic mineral. The pH of the seeded and nonseeded aerobic effluents were 3.8 to 4.1 over the entire hydraulic flow range.

b) Effluent acidity under nonaerobic conditions was solely that contributed by ferrous ion. For aerobic effluents the total acidity is lower for seeded than nonseeded systems at flows providing retention times greater than approximately three hours. This is attributed to consumption of acid by the chemoautotrophic microorganisms. At higher flow rates or lower retention times the total acidity is greater in the aerobic-nonseeded effluents. Acidity, corrected for ferrous ion and expressed as H_2SO_4, decreases as flow increases and retention time decreases from 7 to 1.5 hours for the aerobic-seeded system. The corrected acidity is much greater in aerobic-nonseeded systems at 7 hours retention but decreases to concentrations equivalent to aerobic-seeded systems at retention times of 1.5 hours.

c) Ferrous ion and total iron release is greater from the aerobic-seeded than from the aerobic-nonseeded systems at all retention times greater than 1.5 hours. Most of the total iron content of the effluent is Fe (II). Ferric compounds precipitate in the bed. Mass release of iron reaches a maximum at approximately 2 hours retention time in the aerobic-nonseeded system then remains constant as flow rate increases. For the aerobic-seeded system the iron release reaches a higher maximum value than for the aerobic-non-seeded system at approximately the same hydraulic rate. With increasing flow, lower retention times, there is a drop in mass release of iron until the mass release from the aerobic-seeded and aerobic-nonseeded systems is comparable at 1.5 hours retention time.

d) There is no sulfate in nonaerobic system effluents. For aerobic systems, the sulfate mass release is greater for the seeded than for the nonseeded condition over most of the hydraulic range studied. Maximum release is at approximately 2 hours retention time in each case. For the nonseeded system, increasing flow does not alter the mass release of sulfate. For the seeded system, the sulfate release drops as retention time decreases to 2 hours and approaches the nonseeded system mass release at retention times 1.5 hours. Sulfate required to balance nonferrous acidity, expressed as sulfuric acid, is in slight excess and increases with flow rate for aerobic-nonseeded systems but decreases from a great excess at low flow rates to values comparable to the aerated-nonseeded system at retention times of 1.5 hours.

e) In aerobic systems the mass release of sulfur as sulfate and of total iron approximates the stoichiometric ratio expected from pyritic dissolution; however, because of reaction product accumulation within the pyritic beds, the effluent concentrations are not indicative of the pyrite dissolution rate.

f) The effect of chemoautotrophic organisms on formation of acid mine drainage is the result of a dynamic equilibrium between the rate at which their cells reproduce, their flushout rate within the effluent and the dissolution of pyrite. It is not possible from these results to establish whether these microorganisms directly affect pyrite surface reactions. They enhance oxidation of Fe (II) but the increased Fe (II) in the effluent of seeded systems may be an indirect result of higher ferric:ferrous ion ratios at the mineral surface rather than a direct microbial action.

(5) The standard chemoautotrophic microorganism mixture used to seed the pilot plant systems contained equal numbers of Thiobacillus thiooxidans, Ferrobacillus ferrooxidans and Ferrobacillus sulfooxidans. In tests made at flow rates which provided 4.3 hours retention it was found that the effluent showed little difference in composition whether the seed was the individual organism or the ternary mixture.

(6) When effluent is recycled at 1:1 and 4:1 times the forward flow rate, the mass release of acidity, ferrous ion and total iron and sulfate increases directly with the total flow through the pyritic bed.

Supplemental studies made with flooded, vertical, packed-bed columns of pyrites operated as aerobic-seeded systems demonstrated that:

(7) Forced aeration of the pyritic bed raised acidity 35-fold. The corresponding pH changed from 5.2 to 2.8 in comparison to a nonaerated system. Ferrous ion, total iron and sulfate discharge increased by approximately 30-, 70-, and 120-fold respectively with aeration. Passing gaseous carbon dioxide through the pyritic bed raised the acidity 12-fold. Although pH remained comparable, iron

concentration increased 3- to 4-fold and sulfate only 50%.

(8) If reactant (chemical or biological) depletion or reaction product concentration is not rate limiting, the release of acid mine drainage is proportional to the available pyritic surface area for a given hydraulic flow rate. This relationship does not apply if flow is so low that transport is diffusion rate limited."

From: "Microbiological Leaching of Sulphide Minerals" by Duncan, British Columbia Research Council, Vancouver, B.C., 1967.

"In commercial leaching operations the most readily controlled variable is pH. T. ferrooxidans will oxidize chalcopyrite over the pH range 2.0 to 3.5 and in so doing usually lowers the pH to the vicinity of pH 2. In shake-flask studies the initial pH established the leach rate and subsequent changes in pH did not influence it. The maximum rates occurred when the initial pH ranged from 2.5 to 3.0.

These results indicated that precise control of the leaching pH was unnecessary. However, the problem of precipitation of ferric iron frequently necessitates close pH control.

The list of minerals which can be oxidized by T. ferrooxidans continues to grow. Although both galena and molybdenite have been reported as being susceptible to attack, this has not been confirmed in our laboratory. Certain minerals among those attacked, such as millerite and marmatite are completely broken down but others, most notably chalcopyrite, are only partially oxidized.

Our research work has been principally on chalcopyrite and we find that from 10 to 60% of the copper of some samples cannot be released through microbiological action. The reasons, therefore, are the subject of continuing study.

The sample of tetrahedrite examined released all of its copper into solution through microbiological action, but no silver was solubilized, probably indicating it was present as metallic silver. Assays were not carried out for solubilization of other metal components.

Bryner reported leaching a sample of tetrahedrite but only 2.9 mg of copper was released in 42 days from their sample of unspecified composition.

To date all the nickel sulphides that we have examined have leached completely. The incomplete extraction obtained for a nickel sample examined was attributed to the presence of nickel as the arsenide (loellingite), which was not amenable to biological oxidation.

Like many bacteria, T. ferrooxidans is ubiquitous, and its activities are manifested in leaching wherever a sulphide substrate, oxygen, carbon dioxide, water, certain essential nutrients and the correct pH make up a suitable environment.

Currently, however, commercial processes exist only for the recovery of copper and uranium from leach solutions.

Appreciable quantities of zinc, nickel, cobalt, aluminum and other metals are not being recovered and are frequently lost through leakage and overflow from leaching operations."

Other references used in this section:

(a) "Biological Leaching of Mill Products" by Duncan, Walden and Trussell, Division of Applied Biology, British Columbia Research Council, Vancouver, B.C., 1965.

(b) "Bacterial Extraction of Metal" by Trussell, Walden and Duncan, British Columbia Research Council, Vancouver, B.C., Canada, 1964.

THE CHEMICAL CHARACTERISTICS OF TAILINGS THAT ACT AS A SOURCE OF ACID MINE DRAINAGE

The problem of acid mine drainage in Ontario begins when a mine-mill operation, during the processes of ore comminution and beneficiation, discards, as waste, the various iron sulphide minerals that occur naturally in the ore. These iron sulphides, finely divided as a result of milling operations, are, along with other gangue (non-valuable) materials discharged as a slurry to a natural or man-made settling basin that is commonly referred to as a tailings area. Here, the slurry undergoes a natural solid-liquid separation and, under ideal conditions, the solid particles, including the iron sulphide minerals, are retained within the confines of the tailings area. The clarified liquid escapes the area via a structure called the decant and as seepage through the bases of permeable dams.

In the past, two types of sulphide deposits have not been commercially recoverable in Ontario. One was the relatively low grade, large volume type of deposit and the other was the type of deposit that was characterized by complex fine-grained sulphide assemblages. In general, both of these types of deposits are now being successfully worked.

The low grade, large volume type of deposit generates large volumes of tailings that may or may not contain significant quantities of iron sulphides. The complex sulphide-assemblage type of deposit is frequently associated with large quantities of the iron sulphide minerals which, as stated before, are rejected to tails as waste. Many individual pyritic tailings areas in the Province cover hundreds of acres and many new large ones are expected.

Tailings areas that are well known as acid producers in the Province of Ontario have iron sulphide contents ranging from 2.5 percent to 72 percent. It is suspected that acid mine drainage conditions will occur even when the iron sulphide content of a tailings mass is less than 2.5 percent.

Complex sulphide assemblages frequently require very fine grinding in order to liberate individual sulphide species. The individual species are recovered as separate concentrates by a process called differential flotation. Unfortunately, the iron sulphide minerals in the ore must also suffer the fine grinding procedure. As the grind becomes finer, the relative surface area of each sulphide particle increases. As the relative surface area of each sulphide particle increases, the probability of an acid mine drainage situation increases. Two years ago, a mill grind of 65 percent minus 200 mesh was common. Today, grinds finer than 300 mesh are becoming common.

The iron sulphides, pyrite, pyrrhotite and marcasite are not the only sulphides that are discharged to a tailings area. There are over 125 naturally occurring inorganic sulphides and sulphosalts and many of these are well known 'ore' sulphides. Since mill efficiencies are seldom greater than 97 percent, limited quantities of these sulphides also gain access to a tailings area. The 'ore' sulphides are subject to chemical attack especially under the extreme conditions that are created by the oxidation of the iron sulphides.

Some metals, cobalt and nickel for example, can substitute for iron in the iron sulphide lattice. When the iron sulphide lattice breaks down, these metals also go into solution if the sulphide is in an aqueous environment.

The bulk of any tailings sample taken in the hard-rock mining district of Ontario is composed of one or more of the common rock-forming minerals. These minerals are basically silicates but carbonates and simple oxides, etc., are known.

Tailings samples can be subjected to two basic types of chemical analyses:

(a) The Fusion Analysis

The fusion analysis results in the complete decomposition of the entire tailings sample. Even 'reactive' mineral grains that are completely encased in a 'non-reactive' silicate shell are taken into solution. This type of reactive mineral grain is generally not available to the normal natural leaching processes and its inclusion, in a quantitative sense, in the final sample results may lead to incorrect conclusions. It therefore follows that fusion analyses should never be run on tailings samples if the analytical purpose is to determine the type and quantity of the materials that may or will naturally leach from the samples.

(b) The 'Leach' Analysis

This type of analysis involves an acid attack on the tailings sample and is, in essence, an attempt to leach from the sample only those substances which would or could be removed from the sample under conditions of natural leaching.

The acid mixtures used in this type of attack vary (one common mixture is 3 parts hydrochloric acid to 1 part nitric acid by volume). Acids that will attack silicate minerals (example, hydrofluoric acid) should not be used.

Some typical 'leach type' analyses based on tailings samples from acid producing tailings areas across the Province of Ontario are as follows:

NOTE: All sample results are expressed on a dry-weight basis.

Case #1 (Uranium Operation)

	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
Iron as Fe %	.8	3.1	.7	1.8	1.6	.6
Calcium as Ca %	1.5	.8	.9	.9	1.0	.6
Sodium as Na %	.01	.02	.03	.02	.03	.03
Potassium as K %	1.7	.4	2.0	1.0	.1	1.1
Phosphorus as P %	0.5	.02	.05	.03	.05	.06
Aluminum as Al %	2.7	1.4	3.4	1.0	4.2	1.7
Titanium as Ti %	.1	.1	.2	.1	.1	.1

Case #2 (Copper, Zinc Operation)

	Sample #1	Sample #2	Sample #3
Sodium as Na %	.03	.03	.07
Potassium as K %	.02	.03	.02
Calcium as Ca ppm	2,600	3,870	3,220
Phosphorus as P ppm	16	7.4	26
Cadmium as Cd ppm	33.6	7.8	27.8
Cobalt as Co ppm	122	125	88.2
Manganese as Mn ppm	232	250	352
Iron as Fe %	13	15	9.5
Nickel as Ni ppm	303	310	197
Lead as Pb ppm	0.0	0.0	0.0
Copper as Cu ppm	466	468	1,240
Zinc as Zn %	3.10	0.71	2.71

Case #3 (Copper, Lead, Zinc, Silver, Gold Operation)

	Sample #1	Sample #2	Sample #3
Sodium as Na %	.03	.05	.04
Potassium as K %	.24	.35	.18
Calcium as Ca ppm	1,420	2,770	1,420
Phosphorus as P ppm	53	66	25
Cadmium as Cd ppm	10.8	11.6	18.0
Antimony as Sb ppm	less than 30	less than 30	less than 30
Cobalt as Co ppm	21.1	20.6	35
Manganese as Mn ppm	223	363	218
Iron as Fe %	12	14	20
Nickel as Ni ppm	11.4	17.6	15.3
Lead as Pb ppm	110	130	110
Copper as Cu ppm	901	419	803
Zinc as Zn ppm	3,000	3,000	3,900

Case #4 (Copper, Lead, Zinc, Silver, Gold Operation)

	Sample #1	Sample #2	Sample #3
Sodium as Na %	.02	.05	.05
Potassium as K %	.01	.41	.67
Calcium as Ca ppm	2,000	3,350	2,890
Phosphorus as P ppm	52	35	3.5
Cadmium as Cd ppm	8.0	5.3	6.9
Antimony as Sb ppm	less than 30	less than 30	less than 30
Cobalt as Co ppm	27.3	15.6	16.7
Manganese as Mn ppm	282	288	503
Iron as Fe %	11	9.8	8.4
Nickel as Ni ppm	8.7	10.4	9.9
Lead as Pb ppm	120	92	110
Copper as Cu ppm	500	290	488
Zinc as Zn ppm	3,100	1,700	250

Case #5 (Sulphuric Acid Production from Pyrite)

	Sample #1	Sample #2	Sample #3	Sample #4
Iron as Fe %	25.1	32.6	34.0	46.7
Zinc as Zn ppm	99.3	89.3	235	1,650
Copper as Cu ppm	14.3	12.1	20.3	61.5
Nickel as Ni ppm	99.3	14.2	29.4	65.8
Cobalt as Co ppm	42.5	156	121	180
Arsenic as As ppm	184	94.7	62.7	166
Manganese as Mn ppm	26.7	15.1	24.2	68.4
Cadmium as Cd ppm	0.51	1.4	0.53	8.4

THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF ACID MINE DRAINAGE FLOWS IN ONTARIO

Mine drainage flows that exhibit acid characteristics have a variety of sources on a sulphide or sulphide-associated mining property:

(A) MINE WATER

(a) Conventional Active Underground Mining Operations

Water gains access to underground mine workings in two ways; as downward percolating ground water and as water that is deliberately pumped into the workings by the company for process use.

As a result of faulting, etc., coupled on occasion with diverse solution effects, very sophisticated natural drainage networks can be set up within a particular mineral deposit. Faults, joints, torsion cracks, old drill holes, etc., frequently directly or indirectly connect the mine workings with the surface and thus allow considerable water to flow into the workings. The network can be so efficient, in fact, that a company mining the deposit has to rely heavily on pumps to keep the workings dry. The volume of water that will gain access to a new mine working cannot be predicted. A few mines remain reasonably 'dry'. On the other hand, 'wet' mines are not uncommon. Grouting is required for serious underground flows of water.

The water that percolates through the sulphide or sulphide-associated deposit may bring oxygen, among other substances, into direct contact with the sulphide ore. The sulphides react to produce water soluble salts and sulphuric acid. The water that brought the oxygen to the ore also removes the soluble reaction products from the ore and thus permits the continuation of the reaction. When this solution appears in the mine workings, it is generally characterized by a relatively low pH, a relatively high sulphate content and an abnormal concentration of the various heavy metals.

In appearance, it may be clear and colourless or it may be coloured light-yellow, dark-yellow, amber or rusty-orange. The various colours are due to the state of oxidation of the iron present. If, by chance, cemented backfill is used in the mine, the highly alkaline underflow from backfilled areas will perhaps mask (by neutralization) the original acid characteristics of the mine water but the acid situation within the deposit still exists nonetheless.

Acid underground mine water is, of course, contaminated by the mining process itself. Rock-breaking creates 'fines' that become suspended in underground flows. Trace quantities of the organics (lubricants, oils, etc.) that are associated with mining machinery frequently end up in underground water. A few parts per million of water soluble explosive materials (ammonium nitrate, etc.) are normally detected in underground flows. In fact, any water soluble substance that is taken underground for any purpose can be expected to appear, sooner or later, in the mine water.

All underground water generally flows to one or more underground sumps. The water is pumped from these collection areas to the surface for disposal.

It is important to note that many mining operations subject their collected underground mine water to a degree of waste treatment before it is pumped to the surface. Commonly, some of the suspended solids are removed using various settling mechanisms. The pH may be adjusted for a variety of reasons (equipment protection being the main reason).

The chemical characteristics of mine water vary from mine to mine, from deposit to deposit, and from camp to camp. Under acid mine drainage circumstances, however, each flow will be loosely similar with regard to pH, sulphate content, iron content and overall metals content. However, the geological and mineralogical characteristics of each specific sulphide ore deposit will determine precisely what metals will be in solution, how low the pH will go, and to what extent sulphates and iron will occur in solution.

The following are actual examples of the chemical characteristics of underground mine water in the Province of Ontario. All samples are from properties with known acid mine drainage problems:

Case #1

Type of Operation: Uranium

In this case, sulphides, as such, are not mined. However, the ore does contain significant quantities of iron sulphide minerals. The iron sulphides are treated as valueless material:

	Concentration ppm
Total Solids	6,170
Susp. Solids	15
Diss. Solids	6,155
pH	2.3
Sulphates as $SO_4^{=}$	2,800
Iron as Fe	280
Acidity as $CaCO_3$	3,180
Nitrogen (Nitrate)	102
Nitrogen (Ammonia)	100
Chloride as Cl	621
COD (Chemical Oxygen Demand)	50

Case #2

Type of Operation: Iron

In this case also, sulphides are not mined. However, significant quantities of iron sulphides occur in the ore.

	Concentration ppm
Total Solids	4,180
Susp. Solids	355
Diss. Solids	3,825
Nitrogen (Nitrate)	.36
Nitrogen (Nitrite)	.12
Nitrogen (Ammonia)	6.3
Nitrogen (Kjeldahl)	6.3
Phosphorus (P) Total	.20
Phosphorus (P) Sol.	.13

	Concentration ppm
Sulphates as SO_4	2,280
Acidity as $CaCO_3$	1,600
Turbidity Units	70
pH	2.6
COD	30
Silica as SiO_2	15.5
Sodium as Na	7
Potassium as K	5.1
Calcium as Ca	101
Barium as Ba	less than 1
Lithium as Li	less than .1
Aluminum as Al	49.0
Magnesium as Mg	12
Vanadium as V	4.3
Molybdenum as Mo	less than .5
Total Iron as Fe	960
Chromium as Cr	.15
Lead as Pb	0.0
Cadmium as Cd	0.02
Zinc as Zn	0.97
Silver as Ag	0.0
Cobalt as Co	0.47
Nickel as Ni	0.39
Copper as Cu	0.96
Manganese as Mn	83.0
Tin as Sn	0.00
Titanium as Ti	interference (test not done)
Arsenic as As	0.38

Case #3

Type of Operation: Copper, Zinc, Lead, Silver, Gold

Iron sulphides, treated as a waste material, are an integral part of this sulphide orebody. All four samples, from different sections of the mine, were taken underground at the same mine. Sample #3 represents the underflow from an area of cemented backfill (hence, the high pH).

	Concentration ppm			
	Sample #1	Sample #2	Sample #3	Sample #4
Total Solids	2,200	430	2,200	--
Susp. Solids	130	35	10	--
Diss. Solids	2,070	395	2,190	--
pH	3.9	7.0	11.3	6.8
Sulphates as $SO_4^{=}$	1,136	125	140	--
Total Cu	3.04	0.50	0.03	0.55
Total Zn	16.4	5.2	0.05	18.8
Total Pb	0.0	0.0	0.0	0.0
Total Mn	3.68	0.36	0.0	1.58
Total Cd	0.0	0.0	0.0	0.07
Chloride as Cl^-	11	3	810	--
Free NH_3 as N	15	2.0	16	--
Total Fe	182	6.6	0.0	4.5

(b) Active Open Pit Operations

In Ontario, active open pit operations have not generally given rise to serious water pollution problems. Most active open pits remain relatively dry. The chemical characteristics of any water pumped from an active pit depends on (a) the composition of the ore

(b) the surface area of ore available for chemical attack

(c) the residence time of the water in the pit.

In most cases, water pumped from an active open pit operation will be contaminated. Whether it will exhibit acid characteristics or not will depend on the above-listed factors.

(c) Abandoned Conventional Underground Mines

Abandoned conventional underground mines are generally allowed to flood. Only on very rare occasions will water overflow the shaft collar. In addition, the shaft will generally be capped (hopefully with concrete).

If an abandoned mine is being operated on a caretaker basis and if the workings are kept dewatered, then a continuous or semi-continuous mine water effluent can be expected. This material is generally contaminated.

(d) Abandoned Open Pit Operations

Natural precipitation and ground water flows will usually cause an abandoned open pit to fill or partially fill with water. Only rarely does a visible overflow take place. If the open pit operation resulted in the removal of all original ore then the water filling the pit may be uncontaminated. However, in most cases, the wall rock, at least, contains disseminated sulphides and, as such, the pit water, over a period of years, can become highly contaminated.

It is not unusual for conventional underground operations to follow open pit operations at any particular property. When the property is completely abandoned, the workings may connect.

(B) TAILINGS AREA DECANT

The tailings area decant is generally regarded as the main waste flow from a mining property. It has its primary source in the mill where water is used extensively in the processes of ore comminution and beneficiation. Waste material is discharged from the mill as a slurry (finely-ground rock particles and water). The slurry is directed to a natural or man-made settling basin that is commonly referred to as a 'tailings area'. Here the slurry undergoes a natural solid-liquid separation and, under ideal conditions, the solid particles (including the iron sulphide minerals, if present) are retained within the confines of the tailings area. The clarified liquid escapes the area via a structure called the decant and as seepage through the bases of permeable dams.

Once in a tailings area and after a varying period of time, the iron sulphide minerals, if present, react to form water soluble salts which, when discharged in the effluent from a tailings area, can adversely affect the receiving stream.

Typical acid mine drainage flows are characterized by a relatively low pH, a relatively high iron concentration, a relatively high sulphate concentration and abnormal metal concentrations.

Acid mine drainage situations can only be accurately diagnosed on the basis of detailed chemical analyses of untreated true (see section on seepage flows) seepage flows from tailings areas. Similar analyses of untreated mine water having an origin in the workings from which the ore was recovered are also useful. Under no circumstances, however, should an acid mine drainage situation be diagnosed on the basis of chemical analytical results of tailings area decant *flows from active operations*. On the other hand, decant flows from abandoned operations (these flows result from natural runoff, etc.) may be quite useful as indicators of acid mine drainage problems.

The reasons that an acid mine drainage situation should not be diagnosed on the basis of the decant from an active operation are as follows:

(1) As in any other industry, interruptions in mine-mill operations can and do occur. In general, the chemical characteristics of the tailings area decant more or less directly reflect mine-mill conditions. Obviously, chemical additions (e.g., sulphate) in the mill increase and decrease with fluctuations in production, spills can occur, pumps, etc., can fail, and so on. Unless a person is extremely familiar with the operation of any particular mill, tailings area decant results can be deceptive and frustrating.

(2) The effects of natural precipitation on an *active* tailings area are diverse. If the decant pond is large and essentially covers the entire tailings mass, a degree of dilution will be achieved after a massive rainfall. This in turn causes a 'synthetic' lowering of the chemical concentrations of the tailings area decant for a short but variable period of time. If natural streams gain access to the tailings area, the effect of dilution during and after periods of rain may

be even more significant. If, on the other hand, the tailings area decant pond serving an active operation only occupies a portion of the total tailings area and expanses of sulphidic tailings are exposed to the atmosphere, heavily contaminated runoff from the exposed tails may enter the decant pond and thus negate the effects of dilution at the decant. In cases of this type, short periods of heavy precipitation will actually increase the 'acid' loading from the property.

Abandoned tailings areas, of course, are frequently characterized by great expanses of sulphidic tailings that are exposed to the atmosphere. Complex oxidation reactions ensure that, at all times, copious amounts of water soluble acid producing salts are available to natural leaching processes. During periods of heavy rain, runoff from these areas is grossly contaminated. The result is the generation of 'acid surges' into area watercourses. This aspect of acid mine drainage is, in a sense, duplicated in the coal producing areas of the eastern United States.

(3) Depending on the efficiency of an active tailings area as a settling basin, varying quantities of suspended solids (reactive and non-reactive) are found in the decant overflow. Wind tends to force slimes into suspension.

Quantities of reactive suspended solids (sulphides, etc.) in a sample over a sufficient period of time may initiate reactions that could cause changes in pH, dissolved metal concentrations, etc.

(4) In sulphide mine-mill operations, thiosalts are generated when alkaline solutions come into contact with sulphides (particularly iron sulphides - see "The Chemistry of AMD"). These salts eventually react to produce sulphuric acid (and hence 'sulphate') in the decant pond. It is therefore absolutely essential to distinguish between this form of acid generation that occurs when the sulphide mill is operating or when highly alkaline solutions come into contact with sulphides and the true form of acid mine drainage that can occur both when the property is active and when it is abandoned. Acid mine drainage problems are most serious at abandoned properties or on abandoned sections of active properties.

(5) It is common practice at many mining operations where acid problems occur to add a neutralizing agent (generally lime CaO) at the point of mill discharge. This neutralization operation completely destroys most of the waste characteristics that are attributed to acid mine drainage.

The chemical characteristics of tailings area decants that serve (active and abandoned) mining properties in Ontario that exhibit acid characteristics are illustrated by the following actual examples:

Case #1 (active property)

Type of Operation: Copper-Zinc

Comment: Lime added to mill discharge

The iron sulphides at this property are treated as waste material.

	Concentration ppm
pH 3.0	
Sulphate as $SO_4^{=}$	855
Arsenic as As	0.06
Iron as Fe	11.7
Zinc as Zn	0.43
Copper as Cu	0.0
Chromium as Cr	0.0
Lead as Pb	0.11
Cadmium as Cd	0.00
Cobalt as Co	0.06
Vanadium as V	0.0
Manganese as Mn	0.42
Chloride as Cl^-	8

Case #2 (abandoned property)

Type of Operation: Sulphuric acid manufacture from pyrite ore

Comment: Pyrite 'fines' scattered over entire property. Runoff collected in one area. Overflow from area classed as 'decant'.

	Concentration ppm
pH 2.6	
Dissolved Solids	9,200
Colour Dilution 1:2,500	
Hardness as $CaCO_3$	1,392
Acidity as $CaCO_3$	3,800
Chloride as Cl^-	6
Kjeldahl Nitrogen as N	6
Chemical Oxygen Demand	110
Total Phosphorus as P	.025
Silica as SiO_2	110
Sulphate as $SO_4^=$	4,050
Total Iron as Fe	1,310
Chromium as Cr	0.4
Aluminum as Al	160
Magnesium as Mg	178
Calcium as Ca	454
Lithium as Li	0.05
Mercury as Hg	.00
Silver as Ag	0.0
Zinc as Zn	34
Copper as Cu	2.45
Titanium as Ti	14
Nickel as Ni	6.3
Cobalt as Co	2.7
Manganese as Mn	8.2
Lead as Pb	0.5
Cadmium as Cd	0.12
Arsenic as As	less than 0.02

Case #3 (abandoned)

Type of Operation: Uranium

Comments: Iron sulphides associated with the ore considered as waste.

pH 2.0 to 2.8

	Concentration ppm
Total Solids	13,460
Susp. Solids	25
Diss. Solids	13,435
Sulphates as $SO_4^{=}$	6,900
Total Iron as Fe	220 to 340
Total Ferrous Iron as Fe	90 to 156
Nitrogen (Nitrate)	10
Nitrogen (NH_3)	100
Chloride as Cl^-	97
Chemical Oxygen Demand	278
Uranium as U	5.6
Zinc as Zn	9.4
Nickel as Ni	1.5
Cobalt as Co	1.5
Copper as Cu	2.2
Manganese as Mn	3.6
Titanium as Ti	3.6
Acidity as $CaCO_3$	7,700

Case #4a (active section of tailings area)

Type of Operation: Uranium

Comments: Lime added to mill discharge

	Concentration ppm
pH 6.1	
Chemical Oxygen Demand	11
Total Solids	3,090
Susp. Solids	5
Diss. Solids	3,085
Sulphates as $SO_4^=$	1,560
Total Iron	0.40
Acidity as $CaCO_3$	30
Nitrogen (Nitrates)	68.6
Nitrogen (NH_3)	83
Chlorides as Cl^-	94

Case #4b (abandoned section of tailings area)

Comments: Same property as 4a (above). Treatment not provided.

	Concentration ppm
pH 2.6	
Chemical Oxygen Demand	58
Total Solids	3,840
Susp. Solids	35
Diss. Solids	3,805
Sulphates as $SO_4^=$	2,150
Total Iron as Fe	550
Diss. Iron as Fe	550
Acidity as $CaCO_3$	1,940
Nitrogen (Nitrates)	1.29
Nitrogen (NH_3)	12.0
Chlorides as Cl^-	less than 1.0

Case #5 (active)

Type of Operation: Copper, Lead, Zinc

Comments: Iron sulphides treated as waste. Lime added to mill discharge.

	Concentration ppm
pH 6.4	
Total Solids	1,096
Susp. Solids	18
Diss. Solids	1,078
Acidity as $CaCO_3$	29
Sulphates as $SO_4^=$	670
Magnesium as Mg	16
Manganese as Mn	0.58
Total Iron as Fe	29
Lead as Pb	0.0
Copper as Cu	0.22
Nickel as Ni	0.0
Zinc as Zn	2.15

Case #6 (active)

Type of Operation: Copper, Lead, Zinc, Silver, Gold

Comments: Iron sulphides treated as waste. Lime added to mill discharge.

	Concentration ppm
pH 5.3	
Total Solids	1417.6
Susp. Solids	22.7
Diss. Solids	1394.9
Sulphates as $SO_4^=$	1003.5
Total Iron as Fe	22.7
Zinc as Zn	6.5
Copper as Cu	1.1

(C) SEEPAGE FLOWS

Generally speaking, uncontrolled, untreated acid seepage flows present the greatest single acid mine drainage problem at both active and abandoned sulphide operations in the Province of Ontario. Seepage is generally first seen on a property as it emerges from within a tailings mass at the bases of the permeable or semi-permeable dams that form all or part of the perimeter of the tailings area. Occasionally, when a tailings area is confined wholly or partly by natural contours, seepage will leave the area undetected as ground water through permeable strata that make up the natural contours.

In essence, seepage is water that has percolated a varying distance through a tailings mass. If the tailings mass contains sulphide minerals or, indeed, quantities of any reactive mineral species, then the emerging seepage may be highly contaminated.

Seepage flows should be broken down into two main categories:

(a) True seepage flows

(b) False seepage flows

True seepage flows originate deep within a tailings mass. The source waters of these flows percolate for considerable distances through a tailings mass or are retained within the tailings mass for a significant period of time before emerging at the base of permeable dams as definable entities. If the tailings mass in question contains quantities of 'reactive' substances then, by nature, any true seepage flows being generated within the mass are highly contaminated. If 'reactive' substances are not present in the tailings mass, true seepage flows will not be easily distinguishable from false seepage flows.

The following true seepage sample was obtained from an abandoned tailings area in the Elliot Lake district:

pH	2.0
Sulphate as $SO_4^{=}$	7,440 ppm
Acidity as $CaCO_3$	14,600 ppm
Ferric Iron as Fe	1,450 ppm
Ferrous Iron as Fe	1,750 ppm
Uranium as U	7.2 ppm
Zinc as Zn	11.4 ppm
Nickel as Ni	3.2 ppm
Cobalt as Co	3.8 ppm
Copper as Cu	3.6 ppm
Manganese as Mn	5.6 ppm
Aluminum as Al	588 ppm
Lead as Pb	0.67 ppm
Cadmium as Cd	0.05 ppm
Lithium as Li	0.07 ppm
Vanadium as V	20 ppm
Silver as Ag	0.05 ppm
Titanium as Ti	15 ppm
Magnesium as Mg	106 ppm
Calcium as Ca	416 ppm
Potassium as K	69.5 ppm
Sodium as Na	920 ppm
Arsenic as As	0.74 ppm
Phosphorus as P	5.0 ppm
Chemical Oxygen Demand	270 ppm

The above sample, when taken, was clear, colourless and sparkling in appearance.

One characteristic of true seepage flows is their inherent abnormal heavy metals content. The metals present and their relative concentrations vary from property to property.

True seepage flows are not necessarily colourless and, in fact, are quite commonly tinted yellow or amber. If the proper conditions are existant, true seepage flows may even be deep red in colour.

The volume of most seepage flows fluctuates (a lagging response) on a seasonal basis. The volume, of course, increases during and after periods of heavy precipitation and decreases during extended dry periods. If the flows are not too heavily contaminated with various salts, they may freeze solid during the winter months. The volume of true seepage flows fluctuates less radically on a seasonal basis than does the volume of false seepage flows.

True seepage flows are generated and maintained in several ways:

(1) Atmospheric Precipitation

In most areas of northern Ontario, the annual atmospheric precipitation is in the range of 30 inches. Assuming total retention (which is an invalid assumption), each acre of any particular tailings area will received over 678,000 Imperial gallons per year. Assuming total and uniform runoff (also an invalid assumption), atmospheric precipitation alone could account for a maximum daily flow of approximately 1,800 Imperial gallons per acre.

(2) At the present time, and for the most part, tailings areas occupy depressions that at one time were the site of lakes or very wet swamps. When a lake is inundated with tailings, it does not disappear. It merely exists as a 'ghost' within the tailings mass and occupies the spaces between tailings particles. The watershed that fed the 'former' lake does not disappear either. It now feeds into the tailings area or into the vicinity of the tailings area. If the lake overflowed continuously before tailings deposition, it will overflow after tailings deposition. Generally, however, the overflow will not be noticeable until the tailings area is completely abandoned. We then call the overflow seepage.

(3) Decant ponds create and maintain a hydraulic head across a tailings area. The presence of a decant pond or for that matter any ponded water on the surface of a tailings area ensures seepage flows through permeable structures (natural or manmade).

(4) Springs and streams of natural fresh water that gain access to a tailings area all act to increase and maintain the volume of seepage flows.

True seepage flows occur on both active and abandoned properties. On a typical sulphide property, this type of flow is characterized by a low pH, a relatively high sulphate concentration and an abnormal heavy metals concentration. Manganese, copper, cobalt, zinc and nickel are commonly found in these flows.

The list of the possible anions and cations that can occur in an acid mine drainage type effluent is almost endless. The following (an incomplete list), for instance, have all been detected in acid flows in Ontario:

Aluminum
Arsenic
Cadmium
Calcium
Chloride
Chromium
Cobalt
Copper
Iron (ferrous and ferric)
Lead
Lithium
Magnesium
Manganese
Molybdenum
Nickel
Nitrogen (Ammonia)
Nitrogen (Nitrate)
Nitrogen (Nitrite)
Phosphorus
Potassium
Radium - 226 (uranium operations)
Sodium
Sulphate
Thorium - 228 (uranium operations)
Thorium - 230 (uranium operations)
Thorium - 232 (uranium operations)
Titanium
Uranium (uranium operations)
Vanadium
Zinc

True seepage flows do not have to be as concentrated (with regard to contaminants) as the example given. In fact, the concentration of the various contaminants (anions and cations) fluctuates greatly from property to property. Individual flows may lack specific contaminants for a myriad of chemical reasons.

False seepage flows differ from true seepage flows primarily in their sources of water and the fact that false seepage flows are fed by water that has travelled only a limited distance through a tailings mass. This limited travel results in lower levels of contamination relative to true seepage flows which originate within the same tailings mass.

False seepage flows are generated in a limited number of ways:

(a) Generally by the development of extremely porous and fairly well-defined channels leading from the decant pond (or water ponded on the surface of the tailings area) to the base of a permeable dam. The flow through the channel may be slow (a few gallons per minute) or may be so rapid that a vortex forms on the surface of the decant pond. An isolated depression in the floor of the decant pond may be seen (if the water is clear enough) in the vicinity of the vortex and this depression (termed a "suckerhole") marks the entrance or 'feed end' of the channel. Vortex or not, these "suckerholes" are commonly observed at the bottom of pools of clear ponded water near dams on abandoned tailings areas. Usually only 2 or 3 feet in rough diameter, suckerholes up to 15 feet in diameter and several feet deep have been observed in Ontario.

(b) Tailings area dams (composed of drift, waste rock or classified mill tails) frequently lap onto solid bedrock. The point of contact (horizontal, vertical or inclined) between the dam and bedrock forms an ideal seepage plane. If the plane extends to the vicinity of the decant pond, false seepage may result. In other circumstances, true seepage will result.

(c) Subterranean water sources (springs) frequently are covered by a tailings mass. Should an active spring be located close to a tailings dam, a type of false seepage from the toe of the dam in the vicinity of the spring may result.

The chemical characteristics of false seepage flows may be and generally are significantly different from the chemical characteristics of true seepage flows. While true seepage flows reflect the nature and magnitude of the chemical reactions that are operative within a tailings mass, false seepage flows generally reflect, to a greater or lesser extent, the chemical characteristics of the decant pond (or water ponded on the tailings area) itself. If the decant pond is highly contaminated, the false seepage will be highly contaminated. If the decant pond is only slightly contaminated, the false seepage will only be slightly contaminated.

The following actual examples (all taken from the same abandoned tailings area) illustrate, in part, the differences between and the relationships of the decant pond, true seepage and false seepage.

(a) Decant Pond

pH	3.0
Solids (total)	690 ppm
Solids (suspended)	5 ppm
Solids (dissolved)	685 ppm
Sulphates as $SO_4^{=}$	540 ppm
Chlorides as Cl^-	1 ppm
Chemical Oxygen Demand	less than 10 ppm
Total Iron as Fe	16.0 ppm
Manganese as Mn	1.37 ppm
Copper as Cu	0.18 ppm
Zinc as Zn	9.28 ppm

(b) False Seepage

pH	3.3
Solids (total)	730 ppm
Solids (suspended)	5 ppm
Solids (dissolved)	725 ppm
Sulphates as $SO_4^=$	370 ppm
Chlorides as Cl^-	5 ppm
Chemical Oxygen Demand	15 ppm
Total Iron as Fe	1.8 ppm
Manganese as Mn	1.57 ppm
Copper as Cu	0.09 ppm
Zinc as Zn	0.21 ppm

(c) True Seepage

pH	2.8
Solids (total)	5,910 ppm
Solids (suspended)	330 ppm
Solids (dissolved)	5,580 ppm
Sulphates as $SO_4^=$	3,240 ppm
Chlorides as Cl^-	less than 1 ppm
Chemical Oxygen Demand	120 ppm
Iron as Fe	Total 908 ppm; Dissolved 700 ppm
Manganese as Mn	3.9 ppm
Copper as Cu	0.92 ppm
Zinc as Zn	0.71 ppm

The chemical characteristics of all of the above vary from property to property and are largely dependent upon individual ore characteristics and fineness of grind. However, from property to property, the relative differences of each are somewhat standard.

Under most conditions, true seepage flows are generally free of abnormal suspended solids concentrations as they emerge from within a tailings mass. The filtering action of the tailings mass itself accounts for this. However, because the channel along which false seepage flows within a tailings mass is quite porous, turbidity in a decant pond may on occasion (or continually) be transmitted to the base of dams.

Both true and false seepage flows can be further classified as either "immature" or "mature" flows. The terms "immature" and "mature" refer exclusively to the oxidation state of the iron that is present (in dissolved or suspended form) in the seepage flows. Ferrous iron is considered to be immature simply because it can be oxidized to the more stable (or mature) ferric form. Therefore, if a seepage flow contains only ferrous iron, it is considered to be an "immature" flow. If it contains both ferrous and ferric iron, the flow is still considered "immature". A flow is considered "mature" when it contains ferric species only. On the above basis, true seepage flows from sulphidic tailings areas tend to be highly "immature" (commonly containing up to 50 percent of the total iron as ferrous species) whereas false flows tend to be "mature". On this basis, true seepage flows have, relatively speaking, a greater potential reactivity than false seepage flows. Obviously, immature flows mature by oxidation and, eventually, become fully mature flows. The process of maturing is often accompanied by a colour change. Clear and colourless true flows revert to yellow or amber-tinted flows. A slow increase (due to precipitating iron salts) in suspended solids concentration may accompany the colour change.

The pH of acid seepage flows commonly lies in the range pH 1.8 to 3.8. However, highly contaminated "acid" seepage flows are also known to occur in the pH range above 3.8; for example:

pH	4.6
Solids (suspended)	19 ppm
Solids (dissolved)	3,471 ppm
Sulphates as $SO_4^=$	2,250 ppm
Total Iron as Fe	162 ppm
Zinc as Zn	5.7 ppm
Copper as Cu	0.21 ppm

Generally speaking, the most contaminated seepage flows will exhibit a pH of 3.0 or less.

(D) PONDING OF ACID WASTES

It is not uncommon for acid seepage flows to gain access to stagnant swampy areas in the vicinity of a tailings area or to gain access to rocky basins with essentially no visible overflow. Under these conditions, an unusual evaporation-precipitation-salt concentration effect takes place that is enhanced if the seepage flows feeding the area are intermittent. Incredibly contaminated wastes can result. During periods of heavy precipitation, these areas can be flushed out.

The following are the chemical results of a sample taken from a stagnant area (containing several million Imperial gallons of liquid) that was known to be fed by an intermittent source of acid seepage:

pH	1.9
Solids (total)	28,600 ppm
Solids (suspended)	100 ppm
Solids (dissolved)	28,500 ppm
Sulphates as $SO_4^{=}$	17,400 ppm
Chlorides as Cl^-	trace
Total Iron as Fe	5,100 ppm
Manganese as Mn	5.04 ppm
Zinc as Zn	7.8 ppm
Copper as Cu	3.28 ppm

Commonly, however, the chemical characteristics of the ponded type of waste resemble those of the following examples:

Example #1

pH	2.4
Solids (total)	8,120 ppm
Solids (suspended)	30 ppm
Solids (dissolved)	8,090 ppm
Sulphates as $SO_4^=$	4,800 ppm
Chlorides as Cl^-	less than 1 ppm
Chemical Oxygen Demand	90 ppm
Iron as Fe	Total 768 ppm; Dissolved 768 ppm
Manganese as Mn	5.2 ppm
Copper as Cu	2.0 ppm
Zinc as Zn	0.54 ppm

Example #2

pH	2.5
Sulphates as $SO_4^=$	1,640 ppm
Iron as Fe	560 ppm
Arsenic as As	0.48 ppm

(E) DEVELOPMENT WATER, DEWATERING OPERATIONS

When they are abandoned, underground mine workings generally fill with water.

If a mining company wishes to re-estimate the mineral potential of any specific property that includes abandoned underground workings, one of the first steps taken will generally be the dewatering of the flooded workings. The total volume of the initial discharge depends almost entirely on the total volume of workings to be dewatered. The chemical characteristics of the discharge depend heavily on the chemical composition and 'reactivity' of the ore and/or waste rock penetrated by the workings, the surface area of the workings, and the length of time that the water has been in contact with the ore or waste rock. As a result, this type of waste discharge varies in nature from 'grossly' contaminated to 'uncontaminated'.

Water that is pumped from abandoned workings that penetrate sulphide deposits can be extremely contaminated. Even if massive sections of the original orebody have been removed by former mining activity, the wallrock or waste rock often contain disseminated sulphides. Even if the wastewater is clear and colourless in appearance and exhibits a neutral or near neutral pH, undesirable metals in undesirable concentrations can be present.

Once an abandoned working has been completely dewatered, the pumps generally must continue to operate, if only on an intermittent basis, to keep the workings from reflooding. Whereas the waste resulting from the initial dewatering will be quite contaminated in many cases, the secondary discharges (to keep the mine from reflooding) may be less so due to a much reduced retention time in the workings themselves.

Once a mine has been dewatered, development work (if justified) may commence underground. In some cases, this work may consist only of testing (sampling) the exposed rock faces for mineral values. In other cases, an underground diamond drilling program may be carried out. In advanced stages, drifting, crosscutting and stope preparation, etc., are necessary.

Under the above circumstances, the principal adverse characteristic of the resulting waste discharges tends to be an undesirable suspended solids concentration. Significant metal concentrations may be associated with the suspended solids.

One actual example of a development type waste discharge is the following:

		Concentration ppm
Solids (total)		1,670
Solids (suspended)		1,380
Solids (dissolved)		290
pH	8.0	
Sulphates as $SO_4^{=}$		17
Chlorides as Cl^-		9
Copper as Cu		2.77

(F) WASTEPILE RUNOFF

Wastepile runoff in the coal mining industry is a major problem. In the hardrock mining districts of Ontario, it is a minor problem.

Simply speaking, most hardrock operations generate amounts of coarse material that must be classified as waste. Unless this waste can be utilized as fill underground or used for construction purposes on the surface, it has to be disposed of in large surface dumps. These dumps or wastepiles are exposed to the atmosphere and are therefore frequently washed by rain or melting snow. If the wastepiles contain quantities of 'reactive' minerals, the underflow from the piles may be contaminated. On the other hand, from a chemical standpoint, the underflow may be quite innocuous.

Common sources of mine waste (rock, soil, etc.) are the following:

(a) Before an open pit operation can be brought into production, all overburden in the pit area must be removed. This material is usually composed of a mixture of glacial drift, clay, sand, gravel and muskeg. It is not uncommon for an orebody that is ammenable to open pit methods to be covered by hundreds of thousands of tons of this type of material. However, unless the overburden contains significant quantities of 'float' from the orebody itself, waste storage piles composed of this material will generally not give rise to highly contaminated underflows.

(b) Open pit mining methods themselves usually generate large quantities of waste rock that must be disposed of. This rock is the rock that immediately surrounds the orebody itself. The rock surrounding the orebody may be chemically similar to the ore matrix and classified as waste based solely on an 'assay boundary' or it may be, as a result of a geological condition, an entirely different and perhaps valueless substance. Commonly, however, the waste rock from this type of operation does contain at least disseminations of the principal ore minerals. If the ore minerals are reactive, the underflow from any such waste piles can be contaminated.

(c) Underground development work generates, from time to time, quantities of waste rock. Whether this waste rock is a result of shaft sinking or drifting and crosscutting in barren 'ground', it is generally regarded as a valuable construction material. If the waste rock cannot be used for backfill, or road construction or dyke building, it must be discarded in a surface dump. Again, the chemical characteristics of this waste determine the chemical characteristics of any underflow.

(d) Under some circumstances, ore from a mine may be preconcentrated before the final milling process takes place. The preconcentration step eliminates very low grade fragments of ore and thus improves the grade of the mill feed. The material that is eliminated, although it contains some mineral values, is regarded as waste. This waste is generally stored indefinitely in surface dumps. Heap leaching on a commercial scale of this type of material is possible if enough material on a continual basis is available. Heap leaching in Ontario is, at the present time, practised on a very small scale.

Mill circuits operate efficiently when the grade of the mill feed is steady. If the grade of the mill feed rises temporarily due to unexpected ore conditions in the mine, low grade waste can be used to dilute the feed. In this way, the low grade waste can be used up and the entrained mineral values can be recovered.

Runoff from the 'low grade' type of wastepile can be quite contaminated if the principal mineral species are reactive. For instance, the underflow from a sulphidic 'low grade' wastepile gave the following results upon analysis:

		Concentration ppm
pH	3.2	
Sulphate as $SO_4^=$		1,135
Chloride as Cl^-		7
Arsenic as As		0.08
Iron as Fe		70
Zinc as Zn		15.4
Copper as Cu		3.1
Chromium as Cr		0.0
Lead as Pb		0.07
Cadmium as Cd		0.00
Cobalt as Co		0.24

Vanadium as V	0.0
Manganese as Mn	3.25

(G) WINDBLOWN REACTIVE PARTICLES

The action of the wind on an exposed non-vegetated tailings area cannot be ignored. 'Reactive' tailings particles torn from the surface of a tailings area can be transported great distances through the air. When these particles drop into area watercourses in sufficient numbers, noticeable impairment can occur.

The following is taken from "Principles of Stratigraphy", Volume I, by Amadeus W. Grabau:

> "Deflation is by far the most important work of the wind and its significance can scarcely be over estimated. The lifting of material from a land surface is largely the work of eddies and irregularities of movement of the wind, including many conflicting cross-currents.
>
> The most important are, of course, the eddies of whirlwinds and tornadoes but many minor currents, due in part at least to the irregularities of the surface, are active in lifting the dust and fine sand. The ordinary convection currents of the atmosphere carry this finer material up to great heights. The force, which moves the particle, is due to the direct impact of the wind, plus the friction along its surface. The force of the direct impact varies with the velocity of the wind, and for a given velocity with the cross-section of the particle in the plane perpendicular to the direction of the wind, as well as with the orientation of the particle and it is of course most efficient when a smooth plane is opposed to the wind. The resistance of the particle varies with its mass, i.e., its size and specific gravity and to some extent, its form. In general, the velocity of the wind necessary to carry a spherical particle of given specific gravity varies as the square of the radius and conversely, the radius of a particle which can be supported by wind varies as the square root of the velocity. It was found that a uniform upward current of air will keep suspended quartz grains, the size of which varies with the velocity, as follows:

Velocity in meters per second	Diameter of quartz grain in mm
0.50	0.04
1.00	0.08
2.00	0.16
3.00	0.25
4.30	0.35
5.00	0.41
6.00	0.49
7.00	0.57
8.00	0.65
9.00	0.73
10.00	0.81
11.00	0.89
12.00	0.97
13.00	1.05

From this, the formula $V = Kr$ was deduced, where K is a constant for the conditions of experiment and r the radius of the particle.

As a result of numerous measurements, the conclusion reached was that the average largest size of quartz particles that can be sustained in the air by ordinary strong winds is about 0.1 mm in diameter but the largest particle that can be transported (not held in suspension) is nearer 2 mm in diameter. This represents the limit of ordinary deflation.

The following table gives the approximate size of quartz sand grains moved by varying wind velocities:

Strength of wind in meters per second	Maximum diameter of sand grains in mm
4.5 - 6.7	0.25
6.7 - 8.4	0.5
9.8 - 11.4	1.0
11.4 - 13.0	1.5

These results are only approximate."

Problems due to wind blown tailings have been encountered at nearly every mining camp in Ontario.

Take, for example, the situation at Mine X. A large unbroken expanse (300 acres) of dry sulphidic tailings was exposed to the action of the wind. During the summer of 1968, it became apparent that swampy areas and "pot-hole" lakes located in the vicinity of the tailings area were contaminated although no normal link to the tailings area could be established. The colour changes in these waters were observed to be identical to the colour changes taking place in waters that were directly exposed to the tailings and, therefore, the possibility of the aerial transport of finely divided tailings from the tailings area to the waters in question could not be ignored.

The first step in our preliminary investigation of the airborne tailings was to secure a sample of tailings that we knew had already undergone some degree of aerial transport. Since deposits of wind-blown sand were easily recognizable and readily available in and around the tailings area, we selected this as our sample source.

The following are the actual average analytical results of the samples in question:

Total Iron as Fe - 2.05%
Calcium as Ca - 0.013%
Sodium as Na - 0.006%
Potassium as K - 0.316%
Phosphorus as P - 0.033%
Aluminum as Al - 0.68%
Titanium as Ti - 0.046%

The above values were obtained by leaching the sample and therefore represent the material available to the natural processes of chemical decomposition and reaction. The iron content is, quite unexpectedly, very high. The bulk of the sample was composed of silicon dioxide (an "inert" material in this context).

A sieve analysis was also run on the wind-blown samples and serves, at least, to identify the size fractions that can be moved by the wind at this mining property:

	Retained by No. 10 mesh -	0.021%
Passed by No. 10,	Retained by No. 25 mesh -	0.029%
Passed by No. 25,	Retained by No. 45 mesh -	1.47%
Passed by No. 45,	Retained by No. 100 mesh -	85.3%
Passed by No. 100,	Retained by No. 200 mesh -	11.7%
Passed by No. 200 mesh		1.44%

Assuming that the samples were representative, it is immediately apparent that particles that will not pass through a 45 mesh screen (U.S. Standard Sieve) are generally too large to be subject to aerial transportation. On the other hand, particles that are small enough to pass through a 45 mesh screen will undergo active aerial transportation should the required conditions present themselves.

It is necessary to point out that the above sieve analysis reflects the characteristics of the wind-blown deposits after they have undergone some degree of aerial transport. In other words, we have to assume that most of the fine (-200 mesh) material was removed by wind action from the deposits before we sampled them.

Analysis of the residual -200 mesh fraction revealed that it contained 15.2 percent iron as Fe. In other words, the fine dust that is blown from the tailings area and that eventually settles on the land and in the stagnant lakes and streams in the immediate area could possibly have contained up to 30 percent sulphides.

THE STRUCTURAL CHARACTERISTICS OF TAILINGS MASSES AND THE EFFECTS OF STRUCTURAL FEATURES WITH REGARD TO OXIDATION

The surface of a tailings mass that is producing 'acid' frequently tends to become partially covered with a thin stable reddish-coloured mass of hydrated iron oxides. We call this covering a "Ferruginous Cap". Similar areas on the surface of a tailings area that are encrusted with deposits of white-coloured salts are referred to as "Alkaline Caps".

There is a widely held opinion to the effect that the formation of ferruginous caps on a tailings area is primarily due to the 'in situ' oxidation of iron-bearing sulphides. In other words, the individual sulphide particles are thought to be oxidized as they each remain at a fairly well-defined point within the 3-dimensional structure of the tailings mass.

The subsequent crust (ferruginous cap) formation is therefore easily explained by stating that, as an individual sulphide particle undergoes oxidation (several intermediary reactions occur), it also experiences an increase in volume. The volume increase is due to the bulky and somewhat flocculent type of iron oxide or hydrated iron oxide that forms as the oxidation end-product of the reaction. The oxide acts as an efficient binder of adjacent particles and results in a somewhat cellular, rusty-red coloured coherent mass.

There are several basic flaws in the above explanation of the formation of ferruginous caps.

To begin with, there is a problem concerning the apparent somewhat homogeneous chemical nature of any large tailings mass that results from the milling of any large relatively homogeneous sulphide ore body. In any such tailings mass (generally containing at least 50 to 60 percent minus 200 mesh material), the actual concentration of the various anions and cations present can be expected to initially vary only gradually from one point to another (assuming that the distance between the points is not excessive). Thus, finely divided non-soluble (stable under local conditions) materials being discharged to a tailings area should, in theory, be detectable in approximately equivalent concentrations in any representative sample taken of the tailings area. In other words, if you assume the 'in situ' oxidation of sulphide particles, you must also be ready to assume that the total concentration of iron (not iron sulphide) in tailings sample X will be essentially the same as the concentration of iron in tailings sample Y which was taken within a few feet (in any direction - vertical or horizontal) of sample X (assuming a uniform distribution of sulphides). A sample taken at a depth of 5 feet should have a somewhat similar iron concentration as a sample taken 2 feet vertically above or below it. The concentration of iron in a ferruginous cap should therefore be similar to the concentration of iron a few feet below the cap. However, most sections examined refute the concept that 'in situ' sulphide oxidation results directly in cap formation. As examples, consider the following actual analytical results:

(a) Ferruginous Cap Section

The ferruginous cap and three distinct units could be seen in the cross-section and were as follows:

(1) Ferruginous Cap

(i) thickness - .1 inches

(ii) colour - intense rusty-red

(iii) position - the ferruginous cap formed the surface unit. It was underlain by Layer A.

(iv) chemical characteristics

% Fe	% Ca	% Na	% K	% P	% Al	% Ti
3.1	.8	.02	.4	.02	1.9	.1

(2) Layer A

(i) thickness - 9.5 inches

(ii) colour - light grey but completely mottled with yellow iron oxide.

(iii) position - immediately under the ferruginous cap. Immediately over Layer B.

(iv) chemical characteristics

% Fe	% Ca	% Na	% K	% P	% Al	% Ti
.6	.6	.03	1.1	.06	1.7	.1

(3) Layer B

(i) thickness - 4 inches

(ii) colour - dark grey but riddled with yellow oxide.

(iii) position - immediately under Layer A. Immediately over Layer C.

(iv) chemical characteristics

% Fe	% Ca	% Na	% K	% P	% Al	% Ti
1.8	.9	.02	1.0	.03	1.0	.1

(4) Layer C

(i) thickness - several tens of feet

(ii) colour - dark grey - unaltered tails

(iii) position - Immediately under Layer B

(iv) chemical characteristics

% Fe	% Ca	% Na	% K	% P	% Al	% Ti
1.6	1.0	.03	.1	.05	4.2	.1

Obviously, the ferruginous cap contains significantly more iron (expressed as Fe) than the original (or unaltered) tailings (as represented by Layer C). The layer (Layer A) lying immediately below the ferruginous cap is relatively depleted in iron (expressed as Fe).

Serious enrichments and/or depletions in the surface layers of many sections examined have been noted with regard to the concentrations of specific cations and anions.

There is one plausible explanation of the formation of enriched (or depleted) surficial layers with ensuing cap formation in tailings areas. The explanation is centred around the phenomena of ion migration.

Sulphides, as such, are of necessity relegated to the secondary (but important) role of 'original iron source'. It is the soluble iron salts that are initially and principally the cause of the surficial ferruginous areas of the tailings body.

For example:

Assume that an iron sulphide (pyrite, marcasite, pyrrhotite, etc.) is discharged to a moist oxygenated environment. The first reaction the sulphide (in this case pyrite) will undergo is probably simultaneous oxidation and hydration.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow \underset{\substack{\nearrow \\ \text{free to migrate}}}{2FeSO_4} + 2H_2SO_4$$

The $FeSO_4$ may add $7H_2O$ to become melanterite or it may oxidize and hydrate further to become coquimbite, $(Fe_2(SO_4)_3.9H_2O)$

$$12FeSO_4 + 3O_2 + 36H_2O \longrightarrow 4Fe_2\underset{\substack{\nearrow \\ \text{free to migrate}}}{(SO_4)}_3.9H_2O + 2Fe_2O_3$$

NOTE: Substances composed of weakly ionized cations and strongly ionized anions, such as coquimbite $(Fe_2(SO_4)_3.9H_2O)$, show a pH, on hydrolysis, that is very low, even as low as 1.0.

It is more probable, however, that any $FeSO_4$ present will hydrolyze in the weathering solution to form sulphuric acid and ferrous hydroxide (a greyish to greyish-green gel).

$$FeSO_4 + 2HOH \dashrightarrow Fe(OH)_2 + H_2SO_4$$

Ferrous hydroxide is unstable and readily oxidizes to $Fe(OH)_3$ which loses water to become limonite, goethite and lepidocrocite or, in other words, a mixture of iron oxides, generally of undetermined crystallization and hydration.

$$4Fe(OH)_2 + O_2 + 2H_2O \dashrightarrow 4Fe(OH)_3$$

$$2Fe(OH)_3 \dashrightarrow Fe_2O_3 \qquad H_2O + 2H_2O$$

$$\text{or } Fe_2O_3 \qquad nH_2O + nH_2O$$

Any sulphuric acid formed as a result of the original sulphide oxidation or oxidation of the ensuing by-products may come into contact with more pyrite with which it may react and thereby evolve H_2S, and possibly release fine-grained sulphur if the sulphur is not oxidized in the reaction.

$$FeS_2 + H_2SO_4 \dashrightarrow FeSO_4 + H_2S + S^o$$

Some of the H_2S may be dissolved in water as hydro-sulphurous acid, and some of it may oxidize incompletely and leave elemental sulphur.

NOTE: Sulphuric acid reacts with limestone if present, to produce gypsum. However, during the reaction H_2CO_3

is also evolved.

$$CaCO_3 + H_2SO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + H_2CO_3$$

Concerning the above reactions, the following should be noted:

(a) pyrite as such, is relatively insoluble and therefore is not free (except in very isolated instances) to migrate throughout the tailings body.

(b) pyrite is not oxidized directly to the corresponding oxide and, as such, is not the immediate agent responsible (except under local conditions where quantities of the sulphide have been mechanically concentrated) for the formation of the masses of oxides that form the ferruginous caps.

(c) the immediate oxidation products of the iron sulphides are at least moderately soluble and, as such, are free to migrate throughout the tailings mass.

(d) ferrous sulphate, when oxidized to the ferric state, yields as a by-product, an insoluble rusty-red coloured compound (Fe_2O_3).

(e) ferrous sulphate, when hydrolyzed, yields an unstable hydroxide ($Fe(OH)_2$) which, in an oxidizing environment, yields an insoluble rusty-red coloured compound.

The mechanics of cap formation are therefore theoretically as follows:

(i) capillary action brings relatively dilute salt solutions from the more or less uniform interior of the tailings mass progressively nearer the surface of the tailings body.

(ii) as under desert conditions, loss of moisture at or near the surface of the tailings mass causes a relative increase in the concentration of the salts at or near the surface. As concentration effects increase, specific salts may differentially precipitate.

(iii) the evaporation-salt concentration effect most dramatically affects the ferrous (in general, iron) salts. Conditions within a few inches of the surface of a tailings area are generally strongly oxidizing. As a result, ferrous salts, as they enter this zone, are oxidized to insoluble bulky precipitates that are entrapped by the matrix of tailings particles.

NOTE: As would be expected, there are many "rate-limiting factors" involved in the oxidation of any constituent of the tailings mass. Natural conditions may be quite different from those in the laboratory. Under natural conditions the rate-controlling "reaction" in many cases is not the chemical reaction but a diffusional resistance that limits the rate of sulphide oxidation. If enough oxygen cannot enter the system to react with all readily oxidizable materials, then it would follow that at least a fraction of the oxidizable material will escape the general vicinity of the tailings mass in an unoxidized state even though the material has passed through an ostensible oxidizing zone.

The above appears to be the case at many mines in Ontario.

The local intensity of the oxidation reaction in a tailings area is highly dependent upon the permeability and relative mineral composition of the beds of tails that were laid down as a result of tailings deposition within the basin. The slurry that is discharged from a mill as waste generally contains at least two size fractions: - a sand (relatively coarse) fraction and a silt (relatively fine) fraction. Beds in a tailings area that were either formed relatively close to the discharge point of a tailings line or formed (laid down) in a relatively fast-moving stretch of the slurry stream tend to be sandy with a low silt content. On the other hand, beds composed predominantly of silt sized particles were formed in stagnant areas of the tailings basin or, at least, in an area remote from the source material. Since the slurry stream feeding the tailings area is generally moved occasionally, and because the slurry stream itself meanders aimlessly over the relatively flat surface of the tailings area and continually changes its course, beds of silt and sand are found all over the tailings body and are in no particular continuous vertical or horizontal sequence. The relatively sandy beds tend to have a more open texture and hence permit the percolation of water (and oxygen) throughout themselves.

Favourable conditions for the survival of specific types of iron oxidizing bacteria are therefore set up. The beds composed predominantly of silt sized material tend to restrict the free passage of water (and oxygen). Furthermore, concentrations of clay minerals (which swell on contact with water) in the silty beds close the structure even more. Therefore, the production of a ferruginous cap (stable red-coloured covering) on the surface of the tailings area is much more dependent on whether a silt bed or a sand bed lies at the surface at any particular location, than on the iron content of the beds.

THE STABILITY OF MINERALS

Stability is a relative property. For example, calcite is said to be stable at ordinary temperatures and pressures. So it is, but only in the sense that under specific conditions it remains unchanged indefinitely. Drop it into dilute hydrochloric acid, however, and it is certainly far from stable. Stability must therefore be defined not only in respect to pressure and temperature, but also as regards chemical environment. Strictly speaking, one cannot speak of the stability of a single phase (mineral) in a rock, independent of the associated minerals and the pore fluids. Most discussions of particular minerals or mineral associations assume an indifferent chemical environment, in which stability is a function of physical conditions only.

The decomposition of sulphides in a tailings area frequently creates chemical conditions that adversely affect the stability of many of the non-sulphide mineral species that are present. Although these non-sulphide minerals are, in general, characterized by their relative stability in a natural environment, they do break down very slowly and release anions and cations that help to make up natural background concentrations. In a tailings basin, the enormous overall surface area of the tailings mass itself is such that the slow breakdown of the various non-sulphide minerals becomes significant since the soluble reaction products frequently end up in a concentrated form in the seepage or decant overflow from the area. A few grams of tailings taken from almost any disposal area will contain at least traces of most of the elements known to man. It is for this reason that strict attention must be paid to the type and reactivity of all minerals that occur in or are associated with an orebody.

As an example, the following table indicates the relative amounts of the various elements that could be released if total decomposition of granite and diabase (two very common rocks) took place in a tailings area (total decomposition is highly unlikely):

The Average Amounts of the Elements in Crustal Rocks in Parts Per Million

(omitting the rare gases and the short-lived radioactive elements)

Atomic Number	Element	Crustal Average	Granite	Diabase
1	H	1,400	400	600
3	Li	20	24	12
4	Be	2.8	3	0.8
5	B	10	2	17
6	C	200	200	100
7	N	20	8	14
8	O	466,000	485,000	449,000
9	F	625	700	250
11	Na	28,300	24,600	15,400
12	Mg	20,900	2,400	39,900
13	Al	81,300	74,300	78,600
14	Si	277,200	339,600	246,100
15	P	1,050	390	650
16	S	260	175	135
17	Cl	130	50	
19	K	25,900	45,100	5,300
20	Ca	36,300	9,900	78,300
21	Sc	22	3	34
22	Ti	4,400	1,500	6,400
23	V	135	16	240
24	Cr	100	22	120
25	Mn	950	230	1,320
26	Fe	50,000	13,700	77,600
27	Co	25	2.4	50
28	Ni	75	2	78
29	Cu	55	13	110
30	Zn	70	45	82

31	Ga	15	18	16
32	Ge	1.5	1.0	1.6
33	As	1.8	0.8	2.2
34	Se	0.05		
35	Br	2.5	0.5	0.5
37	Rb	90	220	22
38	Sr	375	250	180
39	Y	33	13	25
40	Zr	165	210	100
41	Nb	20	20	10
42	Mo	1.5	7	0.05
44	Ru	0.01		
45	Rh	0.005		
46	Pd	0.01	0.01	0.02
47	Ag	0.07	0.04	0.06
48	Cd	0.2	0.06	0.3
49	In	0.1	0.03	0.08
50	Sn	2	4	3
51	Sb	0.2	0.4	1.1
52	Te	0.01		
53	I	0.5		
55	Cs	3	1.5	1.1
56	Ba	425	1,220	180
57	La	30	120	30
58	Ce	60	230	30
59	Pr	8.2	20	2
60	Nd	28	55	15
62	Sm	6.0	11	5
63	Eu	1.2	1.0	1.1
64	Gd	5.4	5	4
65	Tb	0.9	1.1	0.6
66	Dy	3.0	2	4
67	Ho	1.2	0.5	1.3

68	Er	2.8	2	3
69	Tm	0.5	0.2	0.3
70	Yb	3.4	1	3
71	Lu	0.5	0.1	0.3
72	Hf	3	5.2	1.5
73	Ta	2	1.6	0.7
74	W	1.5	0.4	0.45
75	Re	0.001	0.0006	0.0004
76	Os	0.005	0.0001	0.0004
77	Ir	0.001	0.006	
78	Pt	0.01	0.008	0.009
79	Au	0.004	0.002	0.005
80	Hg	0.08	0.2	0.2
81	Tl	0.5	1.3	0.13
82	Pb	13	49	8
83	Bi	0.2	0.1	0.2
90	Th	7.2	52	2.4
92	U	1.8	3.7	0.52

The natural background chemical concentrations found in watersheds in mining areas are a result of the natural solubilization of the earth's crust in these areas. If the crust in these areas contains relatively abnormal concentrations of various elements, the elements may be expected to occur in abnormal concentrations in the natural waters of the area. It is interesting to note that many minor elements become trapped or occur in the minerals that form the rocks in any specific location. The chemical-physical decomposition of these rocks (in situ or in a tailings mass) may force the minor elements into solution and hence into area watercourses.

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"Principles of Geochemistry", Third Edition, by B. Mason, John Wiley and Sons, Inc.

THE CHEMICAL DECOMPOSITION OF SILICATES

Silicate materials and quartz generally represent the bulk of discarded material in a tailings area that serves a sulphide mining operation. From a relative standpoint, quartz and the silicates must be regarded as some of the more stable components of the earth's crust. However, under no circumstances should quartz and especially the silicates be regarded as chemically inert.

ANY SOLUTION IN CONTACT WITH SILICATE MINERALS WILL TEND TO BECOME ALKALINE. How alkaline it becomes depends on the nature of the silicates. A restraint on the increase in alkalinity is set by reactions of various forms of silica with OH^-:

$$H_2O + SiO_2 \text{ (quartz)} + OH^- \dashrightarrow H_3SiO_4^- \qquad K = 10^{0.4}$$

$$H_4SiO_4 \text{ (aq.)} + OH^- \dashrightarrow H_3SiO_4^- + H_2O \qquad K = 10^{4.2}$$

These processes ordinarily keep the pH from rising much above 9.

The weathering of silicates is primarily a process of hydrolysis. As a simple example, the mineral forsterite (magnesium-rich olivine) hydrolyzes according to the equation

$$Mg_2SiO_4 + 4H_2O \dashrightarrow 2Mg^{++} + 4OH^- + H_4SiO_4$$

the hydrogen ion from water uniting with the silicate group to form the very weak silicic acid. Surface waters generally contain a little more H^+ than would be present in pure water, because of their dissolved CO_2, and this additional H^+ aids the process of hydrolysis. The carbonic acid may be included in the equation:

$$Mg_2SiO_4 + 4H_2CO_3 \dashrightarrow 2Mg^{++} + 4HCO_3^- + H_4SiO_4$$

When acids that are stronger than carbonic are present, as in the case of an acid mine drainage situation, the reaction becomes simply

$$Mg_2SiO_4 + 4H^+ \dashrightarrow 2Mg^{++} + H_4SiO_4$$

As such, the equation for hydrolysis may be written in various ways depending on the local availability of hydrogen ion. These reactions are almost exactly analogous to reactions that might be written for carbonates:

$$MgCO_3 + H_2O \dashrightarrow Mg^{++} + OH^- + HCO_3^-$$

$$MgCO_3 + H_2CO_3 \dashrightarrow Mg^{++} + HCO_3^- + HCO_3^-$$

$$MgCO_3 + 2H^+ \dashrightarrow Mg^{++} + H_2CO_3$$

The only significant difference is that the weak acid formed in the first two equations consists of ions (HCO_3^-) rather than neutral molecules (H_4SiO_4) which reflects the fact that carbonic acid is stronger than silicic acid. Neither the carbonate nor the silicate reactions are strictly reversible, for at ordinary temperatures the addition of Mg^{++} to a bicarbonate or silicic acid solution gives hydrated compounds rather than the anhydrous salts.

For silicates containing several cations the hydrolysis reaction is less simple than for forsterite because in general the different cations go into solution at different rates. At any stage of partial weathering, silicate grains are coated with an outer shell from which some cations have been preferentially removed, hence which must have a different composition from the mineral as a whole. This outer shell serves to "armor" the interior of a grain and makes the dissolving of most silicates extremely slow.

Aluminum silicates involve the further complication that one product of their weathering is practically always a clay mineral, a compound in which some of the original aluminum and silicon apparently remain combined. The reaction can be symbolized by using K-feldspar as an example of an aluminum silicate and kaolinite as a clay mineral:

$$4KAlSi_3O_8 + 22H_2O \dashrightarrow 4K^+ + 4OH^- + Al_4Si_4O_{10}(OH)_8 + 8H_4SiO_4$$

In summary, the weathering of silicates is chiefly a hydrolysis reaction, making the weathering solution alkaline or at least reducing its acidity, and yielding as principal products cations and silicic acid in solution and clay minerals as residual solids.

NOTE: The solubility of quartz (SiO_2) in water at 25°C and atmospheric pressure has been stated to be between .54 ppm and 11 ppm.

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THE pH PRODUCED BY MINERAL PARTICLES IN CONTACT WITH WATER

The acidity-alkalinity of an aqueous solution is conveniently expressed by the designation, "pH", a number taken originally from the reciprocal of the effective hydrogen ion concentration. At neutrality, pH 7, the effective concentration of H^+ and OH^- ions are both 10^{-7} mols per liter. As the pH becomes less (numbers below 7), the effective H^+ ion concentration becomes greater and the solution becomes more acid. At pH values higher than 7, the effective concentration of H^+ ions becomes less and the effective concentration of OH^- ions is greater, whereby the aqueous solution is alkaline.

Quartz (SiO_2) pulverized in water hydrolyzes to a pH about 6 to 7 which is slightly acid to neutral; the feldspars hydrolyze to produce pH 8 to 10; the amphiboles and feldspathoids 10 to 11. This range in pH values is exceedingly important because of its effect on the relative solubilities of Al_2O_3 and SiO_2 which are also products of the hydrolysis reaction.

At pH 10 and higher, both Al_2O_3 and SiO_2 are relatively soluble and therefore the small amounts of them that are released during hydrolysis at these high pH values are likely to be carried away in solution.

For example, the Al_2O_3 and SiO_2 released from hydrolyzing nepheline and from amphiboles (pH 10-11) are likely to be carried away, unless or until their solutions meet with conditions which either (1) reduce the pH, or (2) evaporate part of the water.

Assume that the pH of a solution derived from hydrolyzing nepheline is reduced from pH 10 to pH 8 (which is quite probable in nature), and observe the effect on the solubility Al_2O_3 and SiO_2. At pH 8 the solubility of Al_2O_3 is reduced to almost nil, but the solubility of SiO_2 is reduced only about one-fourth of what it is at pH 10. It is expected, therefore, that at pH 8 hydrated Al_2O_3 will be precipitated, probably as gibbsite ($Al_2O_3.3H_2O$) or as diaspore or boehmite ($Al_2O_3.H_2O$) the common minerals in bauxite, whereas most or all of the SiO_2 will remain in solution and be carried away.

Mineral Name	pH when pulverized in water
Amphiboles	
Actinolite	11
Hornblende	10
Carbonates	
Calcite	8
Dolomite	9, 10
Siderite	5, 6, 7
Clay Minerals and Al Oxides	
Kaolinite	5, 6, 7
Montmorillonite	6, 7
Boehmite	6, 7
Diaspore	6, 7
Gibbsite	6, 7
Feldspars	
Albite	9, 10
Oligoclase	9
Labradorite	8, 9
Anorthite	8
Orthoclase	8
Microcline	8, 9
Feldspathoids	
Nepheline	10-11
Leucite	10
Micas	
Biotite	8, 9
Muscovite	7, 8
Olivine	10, 11
Pyroxenes	
Aegirite	9
Augite	10
Diopside	10, 11
Hypersthene	8
Quartz	6, 7

Reference:

"The Principles of Chemical Weathering" by W. D. Keller, University of Missouri, 1962.

BACKGROUND CHEMICAL CONCENTRATIONS IN MINING AREAS

"Uncontaminated" fresh water is, in essence, a very dilute solution of salts. The salts have been derived by the slow solubilization of the earth's crust. On the average, "uncontaminated" fresh water contains approximately 100 ppm total salt content.

The kind of salt, the anions and cations, carried by any one stream depends largely on the local or regional climate and on the mineralogical composition of the rock masses that outcrop in or underlie the particular watershed. Near the headwaters of a stream (a typical mining situation), the composition of the water may reflect the composition of adjacent rock masses especially if large orebodies lie at or near the surface of the earth in the immediate vicinity. Away from the area of the headwaters of a stream, the effect of vegetation, of adsorption processes, and of mixing with tributaries very quickly alter the composition to a type largely responsive to the climate. In humid climates, the abundance of CO_2 from decaying vegetation gives stream water a high carbonate content (using "carbonate" to refer to the total $CO_3^{=} + HCO_3^{-} + H_2CO_3$) and makes it acid enough to dissolve limestone fairly rapidly; hence, in streams of humid regions, Ca^{++} is generally the dominant cation and HCO_3^{-} the dominant anion.

In arid regions, on the other hand, CO_2 is not added to the water in sufficient amounts to counterbalance alkalinity produced by hydrolysis; Ca^{++} and $CO_3^{=}$ are largely precipitated out in the B horizons of soils, and stream water is characterized by Na^+ as the dominant cation and either $SO_4^{=}$ or Cl^- as the chief anion.

The waters in the hardrock mining district of Ontario are characterized by a very low dissolved solids content, a low sulphate content and a low metals content. The following actual analytical results give an indication of the type of water that can be expected in the area under natural conditions:

Case #1: Large natural lake (surface area in excess of 20 square miles)

		Concentration ppm
pH	7.2	
Conductivity	58 MHOS	
Dissolved Oxygen		10.1
Total Solids		43
Suspended Solids		1
Dissolved Solids		42
Alkalinity as $CaCO_3$		30.4
Total Hardness as $CaCO_3$		26.6
Chloride as Cl^-		1.06
Sulphate as $SO_4^{=}$		less than 0.6
Total Nitrogen as N		0.296
Total Phosphorus as P		0.014
Copper as Cu		0.023
Nickel as Ni		less than 0.008

Zinc as Zn	0.026
Iron as Fe	0.03

Case #2: Medium-Sized Lake (surface area 9 square miles)

		Concentration ppm
pH	7.2	
Total Solids		50
Suspended Solids		2
Dissolved Solids		48
Sulphate as $SO_4^=$		less than 5
Free Ammonia as N		.01
Total Kjeldahl Nitrogen as N		.24
Nitrite as N		.003
Nitrate as N		.00
Total Phosphorus as P		.008
Alkalinity as $CaCO_3$		17
Acidity as $CaCO_3$		2
Iron as Fe		.05
Zinc as Zn		0.0
Copper as Cu		0.0
Lead as Pb		0.0
Sodium as Na		2
Potassium as K		.7
Calcium as Ca		6
Magnesium as Mg		1

Case #3: River in the vicinity of an orebody (No mining activity)

		Concentration ppm
pH	7.4	
Conductivity	42 MHOS	
Alkalinity as $CaCO_3$		16
Total Hardness as $CaCO_3$		24
Sulphate as $SO_4^{=}$		6.8
Calcium as Ca		6.9
Magnesium as Mg		1.1
Cadmium as Cd		less than 0.004
Copper as Cu		0.040
Iron as Fe		0.03
Lead as Pb		less than 0.005
Nickel as Ni		less than 0.01
Silver as Ag		0.015
Zinc as Zn		0.098

Fish, inhabiting the uncontaminated waters of the hardrock district, do contain metal concentrations in their body tissues. The following analytical results serve as an example:

Fish Species	Weight of Fish (gms)	Tissue Analyzed	Hg	Concentration - ppm Cu	Zn	Cd	Pb	Ni
Perch	230	muscle	.43	0.3	4.3	0.00	0.0	0.0
Perch	250	muscle	.29	0.1	5.7	0.00	0.0	0.1
Perch	320	muscle	.23	0.3	6.0	0.00	0.0	0.0
Sucker	820	muscle	.19	0.3	3.8	0.00	0.0	0.0
Sucker	630	muscle	.12	0.5	5.3	0.00	0.0	0.0
Sucker	550	muscle	.071	0.7	6.9	0.00	0.0	0.0
Sucker	340	muscle	.030	0.3	6.2	0.00	0.0	0.0

DEFINING THE PROBLEM

The present extent and the probable implications of an acid mine drainage situation occurring at any specific property can be reasonably defined as follows:

(a) A very detailed map of the property in question should be prepared. The map should indicate the source, direction, and volume of all flows that enter and/or leave the property. Receiving watercourses should be clearly indicated.

(b) A routine chemical analysis of each flow on the property should be acquired.

(c) Seepage flows from the tailings area, waste storage piles, etc., should be accurately traced. The ultimate destination of all such flows should be known.

(d) A complete SCAN type analysis should be run at least once on all major flows from the property (a SCAN analysis is an analysis in which the chemist has attempted to identify and determine the amount of every 'contaminant' in the flow).

When dealing with an acid mine drainage situation, any analytical results should include pH, sulphates, acidity, iron, copper, zinc, cobalt, nickel, manganese and lead. In addition to the above, any SCAN type analysis should include the following:

aluminum
arsenic
antimony
barium
bismuth
cadmium
calcium
chromium
lithium
mercury
molybdenum
nitrogen (nitrates, nitrites, ammonia, Kjeldahl)
phosphorus
potassium
sodium
tin
titanium
vanadium

If any metal (excluding sodium, potassium, magnesium and calcium) exists in the effluent or effluents from the property in concentrations greater than 1.0 part per million, it should be regarded as a potential source of trouble. It may cause downstream environmental problems. If, on the other hand, several heavy metals (e.g., cobalt, copper, zinc and nickel) occur in the effluent or effluents in concentrations of less than 1.0 part per million but the combined total is greater than 1.0 part per million, the synergistic effect (one ion acting with another) may be (and probably is) great enough to warrant concern.

(e) A complete metals analysis should be run at least once on representative samples of the iron sulphide minerals that occur in the orebody being mined. These minerals, at the present time, generally will be discarded to a tailings area as waste. Chemical decomposition reactions will release any entrained metals.

The same type of analysis could be carried out on representative samples of each of the 'ore' sulphides being mined.

(f) The natural neutralizing capacity of the tailings should be calculated and compared with the calculated 'acid' production potential of the tailings. If the acid production potential is even slightly greater than the calculated natural neutralizing capacity, an acid mine drainage situation is possible.

(g) The duration of an acid mine drainage problem if left unchecked at any specific mining property can be roughly calculated as follows:

- (i) calculate the total quantity of iron that is being removed on a daily basis from the tailings area. This total figure will include the iron contained in all decant and seepage flows.
- (ii) calculate the total quantity of iron that is introduced to the tailings area as a result of
  - (a) iron-containing reagent additions in the mill
  - (b) rod and ball metal, etc., losses in the mill

(c) the discharge of iron-containing mine water to either the milling circuit or to the tailings area

(iii) subtract the total quantity of iron calculated in (ii) from the total quantity of iron calculated in (i).

(iv) the figure arrived at in (iii) essentially indicates the quantity of iron that is daily contributed to the waste flows as a result of the decomposition of the iron sulphide minerals.

(v) calculate the quantity of iron sulphide minerals (FeS_2) contained in the tailings area and on this basis calculate the quantity of 'reactive' iron (Fe) contained in the tailings area.

(vi) divide the quantity of 'reactive' iron calculated in (v) by the quantity of iron indicated in (iii).

(vii) the figure arrived at in (vi) roughly indicates the duration of the acid mine drainage problem expressed in days.

The above calculations can be made quite accurate if, and only if, factors such as the natural neutralizing capacity of the tailings are incorporated into the calculations. Obviously, accuracy will improve as samples become more representative of seasonal effluent conditions.

THE PROBABILITY AND PRELIMINARY SIGNS OF THE DEVELOPMENT OF AN ACID MINE DRAINAGE SITUATION AT ANY SPECIFIC MINING PROPERTY

The development of an acid mine drainage situation at a mining property is probable if:

(a) the ore (including country rock) being milled contains iron sulphide minerals;

(b) the iron sulphide minerals in the ore are being rejected to the tailings area as waste; and

(c) the ore (including country rock) does not naturally contain enough carbonate or similar material to effectively neutralize all the 'acid' that will result from the decomposition of the iron sulphides.

The probability of an acid mine drainage situation increases:

(a) with an increase in fineness of grind in a mill circuit. As the grind becomes finer, the total available surface area for reaction increases.

(b) with an increase in the number of permeable dams on the property or with an increase in the length of existing permeable dams on the property. Seepage flows through the dams act as the transport medium for the soluble reaction products of sulphide decomposition. If the soluble reaction products are not removed, connecting pore spaces in the tailings mass become clogged with these substances and the acid mine drainage mechanisms are forced to slow down because of a lack of available oxygen, water and soluble ferric iron.

(c) with the return of untreated seepage from the bases of dams to the main tailings area. In acid mine drainage situations, untreated seepage contains quantities of dissolved ferric iron. This ferric iron can cause the oxidation of further amounts of iron sulphide should it come into contact with iron sulphide.

(d) with an increase in the surface area of a tailings basin. As a tailings basin expands to cover large areas, seepage water has to move greater distances through the tailings mass in order to escape the area. This in turn results in longer contact times between the percolating (seepage) water and the reactive substances of the tailings mass.

Acid mine drainage symptoms develop long before acid mine drainage becomes the dominant chemical force in a tailings area. These symptoms are best observed in relatively small non-fluctuating seepage flows that emerge from the base of tailings dams on a property. The sulphate concentration, as an example, begins a lazy climb upwards. This can generally be detected by periodic sampling of the same flow over a number of months. The tailings area decant should not be chosen for this type of work since sulphate additions in the mill, which tend to increase as production increases, make the establishment of a base sulphate concentration quite difficult. Also, the decant is fed by wastes that originate in the mill, run across the top of the tailings mass and then leave the area. Seepage, on the other hand, is a result of water percolating through a tailings mass and is therefore in a better position to pick up soluble oxidation products.

Since the sulphate concentration of most natural lakes, rivers and streams in northern Ontario is approximately 10 parts per million, a reading of a few hundred parts per million sulphate in a seepage flow is cause for concern. Readings of 1,000 parts per million sulphate are very common when acid mine drainage conditions are well established. Seepage flows containing in excess of 11,000 parts per million sulphate have been noted in the Elliot Lake district.

An increase in sulphate content usually coincides with a decrease in pH and an increase in the concentration of iron and other heavy metals.

Most acid mine drainage flows are characterized by inherent abnormal metal concentrations. The metals most commonly present are copper, zinc, iron, cobalt, nickel, vanadium, chromium and manganese. As these and other metals begin to appear in effluents for no apparent reason (i.e., they have not been deliberately added to process streams in the mine or mill) an acid mine drainage problem should initially be suspected.

Some symptoms of a developing acid mine drainage situation are very obvious. For instance, acid mine drainage type effluents tend to change colour on standing while exposed to the atmosphere. In most cases, initially clear and colourless, the waste assumes a faint yellow flush which, in time, gradually deepens to intense amber-red. Acid mine drainage reactions also tend to coat exposed portions of a tailings mass with rust-coloured 'caps'.

pH depression in effluents is, of course, the most common indicator of an acid mine drainage problem. When the problem is extremely serious, the pH will tend to stabilize in the range 1.8 to 3.0. In developing (or retarded) cases, the pH will generally fall within the range 3.0 to 5.0.

NEUTRALIZATION OF ACID MINE DRAINAGE

The treatment of acid mine drainage at the present time involves some form of neutralization.

Neutralization procedures, however, are only effective if they:

a) achieve complete control of pH

b) achieve complete control of metallic contaminants

c) achieve complete control of non-metallic contaminants

d) do not, in themselves, contribute to or create an environmental problem.

There is no known single neutralizing agent that can meet all of the above requirements and, as a result, neutralization, in itself, is never the complete answer to an acid mine drainage problem. However, neutralization does form a very significant part of most answers to the problem.

Many neutralizing agents are available. However all but a few are available in all parts of the country, are available in the large quantities required and are available at a cost that can economically be considered.

Generally speaking, the following reagents are available for use:

1) ammonia
2) sodium carbonate
3) sodium hydroxide
4) limestone
5) lime

A) AMMONIA (NH_3)

Because of its toxicity and nutrient properties, ammonia is not recommended for use as an effluent neutralizing agent. Similarly the use of ammonia and ammonium based compounds in a mill circuit should be avoided.

Ammonia and ammonium based compounds are difficult substances to remove from an effluent stream. Biologists tend to state that ammonia and ammonium based compounds should not be present in an effluent if the receiving watercourse is to be adequately protected.

The toxicity of ammonia is dependent on variables which include:

i) the chemical form of the ammonia

ii) co-existent parameters such as pH, bicarbonate alkalinity, CO_2 concentration, temperature and dissolved oxygen

iii) the aquatic species coming into contact with the ammonia

Recommended safe concentrations for ammonia in a receiving watercourse appear to be within the range 0.036 - 0.21 mg. ammonia/litre expressed as N.

B) SODIUM CARBONATE (Na_2CO_3)

Sodium carbonate, once widely used as a pH regulator in the selective flotation of lead-zinc ores, has been largely replaced by lime due to the latter's lower cost and wide availability. Caustic soda (NaOH) is occasionally used in place of soda ash in some lead-zinc flotation operations.

Where gangue slimes are a particularly serious problem, sodium carbonate (sometimes called soda ash) can be very effective in improving both grade of concentrate and recovery. Since sodium carbonate has a dispersing action, difficulty is experienced at times in thickening and filtering flotation concentrates and tailings from sodium carbonate circuits. However this can generally be overcome by the addition of a flocculating agent to the pulp before it enters the thickner.

Sodium carbonate assists the flotation of arsenopyrite and, therefore, can be a useful addition agent where a non-selective bulk sulphide mineral float is desired.

Sodium carbonate, although readily soluble in water, has the unusual property of reaching maximum solubility at the relatively low temperature of 35.4°C (95.7°F). At this temperature, 100 parts of water will dissolve 49.7 parts of sodium carbonate to give a solution containing 33.2% by weight of sodium carbonate.

Sodium carbonate is an acceptable neutralizing agent. Although it will cause an increase in the sodium concentration in the receiving watercourse this is generally not significant. By replacing lime or limestone treatment with sodium carbonate treatment, the hardness of the receiving water is kept to a minimum. Also, there may be an ecological advantage in using sodium carbonate as it will tend to offset any inorganic carbon deficiency in water that may result from discharges of the acid mine drainage type.

Sodium carbonate does not find wide use as a bulk effluent neutralizing agent because of its high cost relative to lime and limestone. Dry storage areas must be provided for this white salt. Sodium carbonate is, however, easy to handle and is generally regarded as being non-toxic to humans.

Solubility Product of Carbonates in Distilled Water

$MgCO_3.3H_2O$	$2.0x10^{-5}$
$CaCO_3$ (Calcite)	$4.5x10^{-9}$
$SrCO_3$	$2.5x10^{-10}$
$BaCO_3$	$1.6x10^{-9}$
$MnCO_3$	$6.0x10^{-11}$
$FeCO_3$	$3.0x10^{-11}$
$CoCO_3$	$1.6x10^{-13}$
$NiCO_3$	$1.4x10^{-7}$
$CuCO_3$	$2.5x10^{-10}$
$ZnCO_3$	$1.5x10^{-11}$
$CdCO_3$	$5.2x10^{-12}$
$PbCO_3$	$8.0x10^{-14}$

C) SODIUM HYDROXIDE ($NaOH$)

Sodium hydroxide (caustic soda) in flotation is used almost exclusively as an alkalinity - control agent in the flotation of gold ores and non-metallic minerals with which lime or sodium carbonate do not perform satisfactorily.

Sodium hydroxide does not find much use as a bulk effluent neutralizing agent because of its relatively high cost.

Solutions of sodium hydroxide, especially warm or hot solutions, tend to be very corrosive. As a result, specialized equipment is necessary when the material is to be handled in bulk. Also caustic in almost any form will produce a burn when in contact with the human body.

D) LIMESTONE

Limestone is an impure sedimentary rock that consists chiefly of calcium carbonate ($CaCO_3$). Many limestones also contain appreciable quantities of magnesium carbonate.

The chemical composition of limestone (and hence lime) depends on the nature of the impurities and the degree of contamination of the original stone. The contaminating materials were deposited simultaneously with the limestone or entered during some later stage.

The following are representative chemical analyses of eight different limestone samples:

CaO	54.54	38.90	41.84	31.20	29.45	45.65	55.28	52.48
MgO	0.59	2.72	1.94	20.45	21.12	7.07	0.46	0.59
CO_2	42.90	33.10	32.94	47.87	46.15	43.60	43.73	41.85
SiO_2	0.70	19.82	13.44	0.11	0.14	2.55	0.42	2.38
Al_2O_3	0.68	5.40	4.55	0.30	0.04	0.23	0.13	1.57
Fe_2O_3	0.08	1.60	0.56	0.19	0.10	0.20	0.05	0.56
SO_3	0.31		0.33			0.33	0.01	

P_2O_5		0.22		0.05	0.04		
Na_2O	0.16	0.31	0.06	0.01	0.01		
K_2O		0.72		0.01	0.03		
H_2O		1.55		0.16	0.23		n.d.
Other		0.29		0.01	0.06	0.08	0.20

i) Solubility of Limestone

High-calcium limestone is only very faintly soluble, so much so that in cold, carbon dioxide-free water it is often regarded as insoluble. Between 17 and 25^oC, its solubility is only 0.014-0.015 gms/litre. As the temperature increases, so does the solubility until at 100^oC solubility increases to 0.03-0.04 gms/litre.

What is the equilibrium pH of water standing in contact with limestone?

For the solubility product of calcite (pure limestone), the most common form of calcium carbonate, we find in tables

$$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^{=}$$

$$K = (Ca^{++})(CO)_3^{=} = 10^{-8.3} = 4.5x10^{-9} \text{ at } 25^oC$$

The solubility in pure water should be the square root of this number, or about $6.8x10^{-5}M$. However, $CO_3^{=}$ hydrolyzes in water so that the process of solution is a bit more complicated:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{++} + OH^- + HCO_3^-$$

For this reaction the equilibrium constant can be evaluated by combining other constants:

$$K = (Ca^{++})\ (OH^-)\ (HCO_3^-) = (Ca^{++})\ (CO_3^=) \times (OH^-)(H^+) \times \frac{(HCO_3^-)}{(H^+)(CO_3^=)}$$

$$= \frac{10^{-8.3} \times 10^{-14}}{10^{-10.3}} = 10^{-12}$$

In pure water the three ions Ca^{++}, OH^-, and HCO_3^- should be formed in equal amounts, so that $(Ca^{++}) = (OH^-) = (HCO_3^-) = \sqrt[3]{10^{-12}} = 10^{-4}$ mole/litre. Hence calcite should dissolve in CO_2-free water to a concentration of 0.0001 M, or about 0.01 gms/litre, and the solution should acquire a pH of 10. However, at such a high pH, the acid HCO_3^- is appreciably dissociated. In fact, the ratio $(CO_3^=)/(HCO_3^-)$ should be about 0.5. This means that the assumption about the equality of the three ions is not valid and that more $CaCO_3$ must dissolve to maintain the ion product at 10^{-12}. Using the rough figure 0.5 for the carbonate-bicarbonate ratio, one could guess that the concentrations of HCO_3^- and OH^- would be about two-thirds of the concentration of Ca^{++}, instead of equal to it, so that the last equation should be:

$$(Ca^{++}) = \frac{3}{2}\ (OH^-) = \frac{3}{2}\ (HCO_3^-) = \sqrt[3]{\frac{9}{4} \times 10^{-12}}$$
$$= 1.3 \times 10^{-4}\ M$$

Thus the solubility is raised to a figure about twice as large as the 6.8×10^{-5} M obtained by simply taking the square root of the solubility product; at the same time the OH^- concentration is lowered slightly so that the pH is approximately 9.9 instead of 10.0.

The corresponding calculation for water containing CO_2 must be based on:

$$CaCO_3(S) + H_2CO_3 \rightleftharpoons Ca^{++} + 2HCO_3^-$$

for which the equilibrium constant is:

$$K = \frac{(Ca^{++})\ (HCO_3^-)^2}{(H_2CO_3)}$$

$$= (Ca^{++})\ (CO_3^=)\ \frac{(HCO_3^-)}{(CO_3^=)(H^+)}\quad \frac{(HCO_3^-)\ (H^+)}{(H_2CO_3)}$$

$$= \frac{10^{-8.3} \times 10^{-6.4}}{10^{-10.3}} = 10^{-4.4}$$

In the reaction:

$$CaCO_3(S) + H_2CO_3 \rightleftharpoons Ca^{++} + 2HCO_3^-$$

2 moles of HCO_3^- are produced for every mole of Ca^{++}. Hence, if there is no other source of these ions,

$$(Ca^{++}) = \tfrac{1}{2}\ (HCO_3^-)$$

For equilibrium with CO_2 in the atmosphere, the concentration of dissolved CO_2 or H_2CO_3 is approximately 10^{-5} M. We can then substitute in the expression for the equilibrium constant:

$$\frac{(Ca^{++})\ (HCO_3^-)^2}{(H_2CO_3)} = \frac{\frac{1}{2}\ (HCO_3^-)^3}{10^{-5}} = 10^{-4.4}$$

whence

$$(HCO_3^-) = 10^{-3.03} = 9.3 \times 10^{-4}\ M$$

The concentration of Ca^{++} in the solution is half this figure, or 4.7×10^{-4} M, more than three times the concentration in pure water. To find the pH of the solution, substitute values for (HCO_3^-) and (H_2CO_3) in the expression for the ionization constant of carbonic acid:

$$\frac{(H^+)\ (HCO_3^-)}{(H_2CO_3)} = \frac{(H^+) \times 10^{-3.0}}{10^{-5}} = 10^{-6.4}$$

whence $(H^+) = 10^{-8.4}$M, and pH = 8.4

ii) Advantages of Limestone as a Neutralizing Agent

The attractiveness of limestone as a neutralizing agent centres primarily on its low initial cost per unit weight and the fact that it presents almost no problems with regard to handling and storage. Also, limestone is usually available on relatively short notice in most parts of the country.

iii) Disadvantages of Limestone as a Neutralizing Agent

(a) The limestone reaction is slow and often requires from 24 to 48 hours to go to completion. The long detention time that is generally required after limestone addition to an acid effluent becomes significant when the land upon which the retention facilities are built is expensive or when numerous impoundment structures are required.

NOTE: Aeration may reduce the retention time.

b) Limestone, under most circumstances, exhibits an inability to effect complete control of dissolved ferrous iron.

The slow reaction in the treatment of calcium carbonate with ferrous iron is explained by a study of the chemistry of the process.

When iron sulfate salts are dissolved in a water medium the compounds undergo hydrolysis reactions to liberate the hydrogen ion. Hydrolysis is defined as a reaction of an ion with water to form an associated species plus H^+ or OH^-. The general equation for a cationic hydrolysis is $M^+ + H_2O \rightleftharpoons MOH + H^+$ so that in the case of iron salts the reactions would be for ferrous iron:

$Fe^{+2} + H_2O \rightleftharpoons FeOH^+ + H^+$ and

$FeOH^+ + H_2O \rightleftharpoons Fe(OH)_2 + H^+$

and the net reaction would be $Fe^{++} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^+$ and for ferric iron

$Fe^{+3} + H_2O \rightleftharpoons Fe(OH)^{+2} + H^+$

$Fe(OH)^{+2} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+$

$Fe(OH)^{+2} + H_2O \rightleftharpoons Fe(OH)_3 + H^+$

the net reaction being

$$Fe^{+3} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$$

These are equilibrium reactions and will go to completion (i.e., completely hydrolyzed) only if the hydrogen ion is pulled out of the equilibrium. This can be accomplished by neutralizing the proton with a base.

Calcium carbonate in an acidic medium will undergo a reaction to form lime and carbon dioxide according to the equation:

$$CaCO_3 + H_2O \rightleftharpoons CaO + H_2CO_3$$

where $H_2CO_3 \rightleftharpoons H_2O + CO_2$

The lime will react with the acid proton to neutralize it and form water plus the calcium salt of the protonic acid:

$$CaO + 2H^+ \longrightarrow Ca^{++} + H_2O$$

For the case of ferric sulfate: The reactions would be $Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2Fe(OH)_3 + 3H_2SO_4$ and $3CaO + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O$. The reaction of calcium carbonate with an acid to form lime will occur just above pH 7 and the precipitation of ferric hydroxide occurs around pH 5.5. Therefore as $CaCO_3$ is added to the acidic $Fe_2(SO_4)_3$ solution, lime is liberated to neutralize the acid formed by hydrolysis and to precipitate the ferric hydroxide.

Ferrous hydroxide will not completely precipitate from the water solution until a pH = 9.5-10 is reached. Since the natural pH of calcium carbonate solution is around pH = 8 and since carbon dioxide must be liberated from $CaCO_3$ in acid to produce lime, it is not surprising that, as any free acid generated by the partial hydrolysis of ferrous iron is used by $CaCO_3$ to form lime, the pH rises above pH 7, stops the reaction of $CaCO_3$ to form lime as well as the complete hydrolysis of the ferrous salt to form hydrogen ions, and eliminates the possibility of precipitating ferrous hydroxide from the solution. If lime instead of $CaCO_3$ is used, the pH will rise to around pH 10 and all of the ferrous iron should be precipitated.

c) During the neutralization process, limestone particles become coated with insoluble reaction products (principally calcium sulphate). If this coating is not continuously removed, the reaction is retarded. In order to remove the coating, mechanical abrasion, etc., is required.

d) The limestone reaction seldom goes to completion. Total utilization of the potential alkalinity of limestone has been known to drop to approximately 31 percent (in contrast, the utilization efficiency of lime is generally in excess of 97 percent). The sludge that results from limestone neutralization contains, in most cases, a residual alkalinity that is of questionable value.

e) Neutralization with limestone tends to become inefficient above pH values of 4.0. pH's above 7.0 are obtained and maintained with some difficulty. pH's above 8.0 are almost impossible to achieve.

In an acid mine drainage situation, neutralization serves two main purposes:

(1) creates and maintains a pH or pH range that will have little or no effect on the aquatic environment; and

(2) causes the precipitation of undesirable substances that occur in the waste streams. These substances are generally ions of the metals although some of the ions of the non-metals also respond to this type of treatment.

If a neutralizing agent (for example, limestone) cannot achieve pH's much in excess of 8.0, then proper control of undesirable substances in waste streams through pH control becomes impossible.

f) The limestone neutralization reaction takes place at the particle surfaces. Therefore, in order to achieve any significant degree of efficiency, the limestone particles must be very small. As a result, a grinding plant is almost a necessary feature of a limestone neutralization plant.

However, as the grind of the limestone becomes finer the cost of the limestone powder (or slurry) increases.

g) The neutralizing action of limestone is described as follows:

$$CaCO_3 + H_2SO_4 \dashrightarrow CaSO_4 + CO_2 + H_2O$$

The production of carbon dioxide, which may stay in solution as carbonic acid, may buffer the reaction and thus hinder the neutralization process in the pH range above 4.6.

h) One dubious advantage (listed here as a disadvantage) of the limestone reaction is that it is not very sensitive quantitatively and therefore the accuracy with which limestone is fed into an effluent stream need not be controlled to the same degree as that required by lime.

In general, fixed beds of limestone are not recommended for neutralization of final effluents. A short time after neutralization commences the individual components of the bed become coated with relatively insoluble reaction products and, as a result, very little is accomplished. Only in a dynamic system are reactive surfaces continuously renewed.

The type of reactions that describe the limestone process are as follows:

i) $CaCO_3 + H_2SO_4 \dashrightarrow CaSO_4 + CO_2 + H_2O$

ii) $3CaCO_3 + Fe_2(SO_4)_3 + 3H_2O \dashrightarrow 2Fe(OH)_3 + 3CaSO_4 + 3CO_2$

iii) $CaCO_3 + FeSO_4 + H_2O \dashrightarrow Fe(OH)_2 + CaSO_4 + CO_2$

iv) $Al_2(SO_4)_3 + 3CaCO_3 + 3H_2O \dashrightarrow 3CaSO_4 + 2Al(OH)_3 + 3CO_2$ etc.

(E) Lime

The term 'lime' has a broad connotation and, unfortunately, is frequently employed in referring to limestone. According to precise definition, however, lime can only be a burned (strongly heated) form of limestone: 'quicklime', 'hydrated lime' or 'hydraulic lime'.

Essentially, these products are oxides or hydroxides of calcium and magnesium, except hydraulic types in which the CaO and MgO are chemically combined with impurities. The oxide is converted into a hydroxide by slaking; an exothermic reaction in which the water combines chemically with the lime. These reversible reactions for both high calcium and dolomitic types are shown diagrammatically below, including calcination:

Quicklime

$$\underset{\substack{\text{high-calcium}\\\text{limestone}}}{\overset{100}{CaCO_3}} + \text{heat} \rightleftharpoons \underset{\substack{\text{high-calcium}\\\text{quicklime}}}{\overset{56}{CaO}} + \overset{44}{CO_2}$$

100 84 56 40 88

$CaCO_3.MgCO_3 + heat \rightleftarrows CaO.MgO + 2CO_2$

dolomitic limestone dolomitic quicklime

Hydrated lime

56 18 74

$CaO + H_2O \rightleftarrows Ca(OH)_2 + heat$

high-calcium quicklime high-calcium hydrate

96.3 18 74 40.3

$CaO.MgO + H_2O \rightleftarrows Ca(OH)_2.MgO + heat$

dolomitic quicklime dolomitic hydrate

96.3 36 74 58.3

$CaO.MgO + 2H_2O \rightleftarrows Ca(OH)_2.Mg(OH)_2 + heat$

dolomitic quicklime dolomitic hydrate

In most types of dolomitic quicklimes, when hydrated under atmospheric conditions, all the CaO component readily hydrates but very little of the MgO slakes. The result is a dolomitic monohydrate or a combination of hydroxide and oxide. However, when dolomitic quicklime is hydrated under pressure or is subject to long retention periods, most of the MgO hydrates to form a so-called highly hydrated dolomitic lime.

Hydraulic limes that are sold in the hydrated form possess considerable impurities (primarily silica, alumina and various iron oxides) that are chemically combined with the lime to form tricalcium silicate, tricalcium aluminate, tetracalcium ferroaluminate, and calcium sulfatoaluminate. Thus, a highly hydraulic lime may possess only 10-35% free (or available) lime. In the relatively pure commercial limes, the available lime content of quicklime will range between 88 and 94% and the total oxide content (CaO + MgO) will be 92-98% in North America. The average purity of limes in Europe, South America, and elsewhere is generally not as high.

There are no solubility values for quicklime because before solubility commences the oxide is hydrated to its hydroxide. The magnitude of solubility of a high-calcium hydrate is 1.330 gms CaO/litre of saturated solution at $10^{\circ}C$ in distilled water (or 0.13%). Thus, lime is about seventy-five times more soluble than high-calcium limestone on a comparable basis and can be regarded as slightly soluble at low temperatures. Contrary to limestone in CO_2-free water, the solubility of hydrate is in inverse proportion to

NOTE: High-calcium limestones decompose into lime at temperatures near $898^{\circ}C$ (1 atmosphere pressure); dolomitic limestones at temperatures near $725^{\circ}C$.

temperature, decreasing with rising temperatures. The presence, in solution, of many inorganic salts such as $CaCl_2$, NH_4Cl, NaCl, etc., increase lime's solubility in varying degrees up to threefold. Alkalies, notably Na_2CO_3 and NaOH, exert an adverse effect, rendering lime almost totally insoluble at elevated temperatures. However, the greatest stimulant to solubility are certain organics like glycerin, phenol, and sugar. Sugar exerts the greatest influence of all. In a 35% sugar solution at 25^oC, 10.1 gms of CaO/100 cm^3 can be dissolved (100 times the solubility of lime in distilled water).

Although data on the solubility of magnesium hydroxide are discordant, the solubility is extremely low. The extent of $Mg(OH)_2$ solubility is approximately 0.01 gms/litre, which is about a hundred times less than the solubility of $Ca(OH)_2$. In concentrated solutions of NH_4Cl and $(NH_4)_2CO_3$, the solubility of $Mg(OH)_2$ is markedly increased. However, in no instance will its solubility equal that of $MgCO_3$ in water heavily permeated with CO_2. Dolomitic hydrates are slightly less soluble than high-calcium hydrates, but much nearer the latter in value than $Mg(OH)_2$, since the presence of MgO and $Mg(OH)_2$ does not impede the dissolution of its $Ca(OH)_2$ constituent.

Quicklime and hydrated lime are reasonably stable compounds but not nearly as stable as their limestone antecedents. Chemically, quicklime is stable at any temperature, but it is extremely vulnerable to moisture. Even moisture in the air will slake lime into a hydrate. As a result, an active high-calcium quicklime is a strong desiccant. Probably, the hydrate is more stable than quicklime. Certainly it is less perishable chemically since water will not alter its chemical composition. Its perishability can only be jeopardized by its strong affinity for carbon dioxide that causes recarbonation. Dolomitic quicklime is less sensitive to slaking than high-calcium quicklime, and dead-burned forms are completely stable under moisture-saturated conditions. Except for dead-burned dolomite, all limes are much more reactive with acids than limestone. The high-calcium types are the most reactive of all.

When quicklime (CaO) is wetted with water it cracks, evolves steam with the evolution of much heat, and falls to a fine white powder of calcium hydroxide ($Ca(OH)_2$) or 'slaked lime'. 'Slaked lime' forms 'milk of lime' when shaken with water; the decanted clear liquid is 'lime water'.

Lime, particularly the high-calcium type, reacts with carbonates such as Na_2CO_3 and Li_2CO_3, to form other hydroxides and carbonates through double decomposition as follows:

$$Na_2CO_3 + Ca(OH)_2 \dashrightarrow 2NaOH + CaCO_3$$

The $CaCO_3$ precipitate can be separated with relative ease from the other soluble reactant.

Lime ionizes readily in water into Ca^{2+}, Mg^{2+}, and OH^- ions, forming a strong base or alkali. Both $Ca(OH)_2$ and $Mg(OH)_2$ are diacid bases, and only one molecule of either is necessary to neutralize such strong monobasic acids as HCl and HNO_3 yielding neutral salts and heat, as displayed below:

$$Ca(OH)_2 + 2HCl \dashrightarrow CaCl_2 + 2H_2O + 27{,}400 \text{ cal}$$

$$Mg(OH)_2 + 2HNO_3 \dashrightarrow Mg(NO_3)_2 + 2H_2O + 27{,}400 \text{ cal}$$

With a dibasic acid, like H_2SO_4, equal molecules of each reactant are necessary for complete neutralization.

$$Ca(OH)_2 + H_2SO_4 \dashrightarrow CaSO_4 + 2H_2O + \text{heat}$$

Reactions involving iron are as follows:

$$2FeSO_4 + 2Ca(OH)_2 \dashrightarrow 2Fe(OH)_2 + 2CaSO_4$$

$$2Fe(OH)_2 + H_2O + \tfrac{1}{2}O_2 \dashrightarrow 2Fe(OH)_3$$

The reaction rates of high-calcium hydrated lime and of dolomitic lime, although very rapid, are slightly retarded by insoluble calcium sulphate. However, the formation of calcium sulphate is less when dolomitic lime is present, because magnesium sulphate is soluble in water.

Lime solutions easily develop a high pH (approaching pH 13 at maximum lime solubility at $0^\circ C$). In uncontaminated water, a pH of 11 is easily achieved using just a trace of lime (calcium carbonate may attain a pH of 8 to 9 and dolomitic stone about 8.5 to 9.2). Lime is the most commonly used alkalinity or pH regulator in the mining industry. It is generally used in the form of slaked lime $Ca(OH)_2$.

The quantity of lime required in any operation varies considerably depending on the pH desired and the extent to which naturally occurring lime consuming constituents are present in the ore.

The maximum solubility of pure lime in cold water is approximately 2.9 lbs. CaO per ton of water, or 1.4 grams CaO per litre. Commercially available lime varies in free lime content from as low as 50% or less to a high of 99%, depending upon the purity of the original limestone. Available CaO content can be determined analytically.

The preferred method of feeding lime is to prepare a slurry of milk of lime containing about 20% finely ground lime together with 80% water by weight. This slurry can be made directly from burned lime if the lime is pulverized; if not, the slurry is usually prepared by passing the burned lime through a small ball or pebble mill operated in closed circuit with a classifier.

Lime is also often fed as a dry solid by means of a slowly moving belt or disc type feeder. This may be done in cases where lime is added to the grinding mill.

Lime usually has a flocculating effect on ore slimes while soda ash tends to act as a dispersant for such slimes. Lime is cheaper than soda ash in most areas and for this reason is widely used for the treatment of sulphide ores; particularly those of copper and zinc. Generally, soda ash is preferred for the treatment of lead sulphide ores and precious metal ores; lime tends to depress galena and metallic gold and needs much more careful control in its addition than does soda ash.

In addition to being an alkalinity regulator, lime is a depressant for the iron sulphides such as pyrite, pyrrhotite and marcasite and for arsenopyrite and for cobalt and nickel sulphides. In this application, lime is often used in conjunction with cyanide.

i) Disadvantages of Lime as a Neutralizing Agent

The main disadvantage of lime is that, on a weight basis, it is more expensive than limestone. It has been reported however that, under some circumstances, the overall cost of limestone will exceed that of lime.

The storage of lime does present some problems. Unlike limestone, lime cannot be stored in the open. A dry storage building must generally be provided (keep in mind however that most sulphide operations are designed with reagent storage areas).

ii) Advantages of Lime as a Neutralizing Agent

(a) Lime is a very reactive material. The neutralization reaction is rapid and goes to completion in less than one hour (the limestone reaction generally requires from 24 to 48 hours to go to completion).

(b) Dissolved ferrous iron can be easily controlled with lime.

(c) The lime neutralization reaction is not significantly retarded by the formation of relatively insoluble reaction products.

(d) The utilization efficiency of lime is generally in excess of 97 percent.

(e) pH's in excess of 8.0 can be easily attained and maintained with lime. Hence, contaminants that respond to a neutralization-type reaction can be controlled with relative ease.

(f) The complex grinding equipment that generally forms a necessary part of a limestone plant is generally not required in the lime plant.

A typical result of lime neutralization is as follows:

	Raw Waste ppm	Treated Waste (lime to pH 8.7) ppm
Total Solids	4,180	3,880
Susp. Solids	355	10
Nitrogen (Nitrate)	.36	3.5
Nitrogen (Nitrite)	.12	.05
Nitrogen (NH_3)	6.3	4.5
Nitrogen (Kjeldahl)	6.3	5.5
Total Phosphorous	.20	.02
Soluble Phosphorous	.13	.01
Sulphates as SO_4	2,280	2,140
Acidity as $CaCO_3$	1,600	14
Turbidity Units	70	--
COD	30	8
pH	2.61	8.7
Silica as SiO_2	15.5	1.3
Sodium as Na	7	9
Potassium as K	5.1	5.6
Calcium as Ca	101	712
Barium as Ba	less than 1	less than .05
Lithium as Li	less than 1	0.00
Aluminum as Al	49.0	0.14
Magnesium as Mg	12	171
Vanadium as V	4.3	interference
Molybdenum as Mo	less than .5	less than .5
Iron (Total)	960	0.24
Chromium as Cr	.15	0.00
Lead as Pb	0.0	0.0
Cadmium as Cd	0.02	0.00

	Raw Waste ppm	Treated Waste (lime to pH 8.7) ppm
Zinc as Zn	0.97	0.02
Silver as Ag	0.0	0.00
Cobalt as Co	0.47	0.0
Nickel as Ni	0.39	0.0
Copper as Cu	0.96	0.0
Manganese as Mn	83.0	9.1
Tin as Sn	0.00	0.0
Arsenic as As	0.38	0.0

Sludge Formation

As stated before, neutralization procedures are only effective if they:

(a) achieve complete control of pH

(b) achieve complete control of metallic contaminants

(c) achieve complete control of non-metallic contaminants

(d) do not, in themselves, contribute to or create an environmental problem.

A neutralizing agent accomplishes (b) and (c) above by forcing specific metallic and non-metallic species in the waste stream into the form of relatively insoluble precipitates. These precipitates, depending on their physical-chemical properties, under quiescent conditions, settle to form a mechanically stable or unstable layer of sludge.

From: The Control and Properties of Sludge produced from the Treatment of Coal Mine Drainage Water by Neutralization

Processes by H. L. Lovell, May 1970, Pennsylvania State University, University Park, Pa.:

In neutralization processes treating coal mine drainage, iron and aluminum species along with some sulfate are formed as hydrolyzed insoluble materials and must be removed from the water. The separation, handling and disposal of such sludges comprises a costly and troublesome part of the treatment process. Sludge control includes the solid-fluid separation from the treated water and possibly one or more sludge dewatering stages. It may also require handling of a sludge as a slurry, wet mud or as a solid. Storage-disposal procedures must be developed. Each of these facets must be coordinated with the process, the site, the raw water quality and the anticipated treatment period. The settling pond-lagoon or a mechanical clarifier is employed to permit sedimentation of the sludge and allow discharge of a non-turbid effluent. The basis of choice between these approaches is one of economics and land availability. In addition, either will serve as a surge capacity to minimize effluent quality variation and to prevent accidental release of unacceptable waters.

Sludge Control

The settling lagoon operation follows two general practices:

(1) The lagoon is designed to serve as both a solid-fluid separator and as a sludge storage area. This procedure may have an economic advantage in capital cost with minimum operating cost but requires extensive land area and provides the least control over accidental contaminant discharges. It probably is the least realistic as an overall conservation approach. Major advantages for each of these factors accrue when two ponds are available. Parallel ponds, each having sufficient retention time to control the entire flow, appears superior in most situations. This design, with the ponds used alternatively, permits the sludge in one to further compact and even dry. However, the drying process under these conditions is usually incomplete.

(2) The lagoon serves primarily for sludge separation and the storage function is limited by periodic sludge removal. This practice reduces land requirements but demands more detailed engineering and possibly higher capital costs. Certainly, operating expenditures will be greater. The higher costs are related to sludge removal. Ready access to the sludge with a pump suction suggests unrealistic pond shapes (long, narrow and shallow). The lagoon process providing for temporary sludge storage and subsequent removal is but one step away from the mechanical clarifier which involves least space, minimal storage and continuous sludge

removal. A pond or lagoon can also be made to function in this manner. The concept of multiple stage solid-fluid separation and dewatering involving both parallel and series stages may be the most satisfactory: The settling lagoon designed for effective solids separation without excessive sludge storage is followed by a protective pond or polishing stage. The sludge thus separated may then be transferred to a second stage dewatering process. The use of a mechanical flocculator at the entrance of a lagoon has been cited to enhance sludge settling time and thus permit reduction in pond size.

Experience in the use of mechanical clarifiers for these purposes has been limited but is usually assumed to be the more costly approach (a situation deserving further evaluation). A mechanical clarifier becomes essential when land area and/or location problems become critical. The versatility in using such a device is especially desirable although no storage concepts can be included beyond short time surge capacity.

Sludge handling may be grouped into three areas: (a) sludge removal procedures (b) sludge transportation and (c) sludge disposal. Sludge removal by a portable, centrifugal pump on the side of the lagoon through a manually-manipulated hose has practical limitations. In addition to labour costs and a manually-difficult job, the speed of pumping the sludge from the pond bottom is partially controlled by the sludge flow ability toward the pump suction. "Rat-holing" may occur as the supernatant water moves more rapidly than the sludge. Thus, the rheological properties (involving particle characteristics, viscosity and temperature) of the sludge become important. Enhanced accessibility within a pond has been achieved by a pontoon-mounted pump moved by an outboard motor directed from the bank. A sludge collection system in which a sludge removal pipe was moved manually along a track mounted in the bottom of a long settling lagoon has been described. Provision for a permanent sludge sump with pumps to empty lagoons has been cited but not detailed. Pipe scaling can be a severe problem and tends to favour the use of open sluices.

Sludge slurries have been transported by tank trucks (and have been pumped short distances by pipeline). The transportation of dry sludge by truck has not been reported but represents the most ideal condition. The usual characteristics of truck capacity, costs and distance prevail. Two sludge properties are especially significant in its transportation: Solids content and the build up of scale. Relatively small weights of solids are handled per gallon of sludge.

Sludge disposal may eventually create solid waste problems and can lead to further pollution problems.

Sludge Properties

These sludges have no known use and are generally non-uniform as well as highly variable in composition. They reportedly have been considered for use as pigments, catalysts building materials, and soil supplements. For other uses, such as basic raw materials, the available quantities and impurity levels have precluded serious investigation. Sludges usually have a high water content (related to the hydrated character of their compounds) and do not readily lend themselves to compaction or drying. Drying or freezing will destroy the structures of the hydrated species and they do not readily rehydrate. It is generally believed that the most highly oxidized state is desired in terms of sludge stability and resistance to further pollution capability. In addition to hydrated oxides of iron (II), (III) and aluminum (III) with varying sulfate content, some sludges may also contain calcium sulfate, alkalies and numerous trace constituents such as silica and metal salts.

Although proper sludge control is dependent upon the properties of the sludge, little detailed information has been reported. These characteristics include chemical composition of the solids as well as the physical properties of the sludge. Both determine the various forms of sludge and thus establish levels of hydration, moisture content, settling rates, compaction characteristics, rheology and surface properties which control the flocculation-agglomeration behaviour.

Chemical Properties of Mine Drainage Sludge

The chemical composition of the sludge is dependent upon the composition of drainage waters, the reagents and processes employed. The concentrations of iron (including ferrous/ferric ratio), aluminum and sulfate and to a lesser extent calcium, carbonate, bicarbonate and dissolved oxygen may be significant. Numerous minor and trace constituents such as silica, phosphates, manganese, titanium, copper, zinc, etc., from the waters may also appear in the sludge due either to their chemistry or physical occlusion. The oxidation state of the iron is probably the basic criteria in establishing the treatment process and whether an oxidation step is necessary. Iron (III) will begin to precipitate with most alkalies near pH 4.0 and will reach residual concentration levels at pH values between 6 and 7.0. In a large capacity system, adequate mixing times must be established to insure an equilibrium situation, despite the fact that these are ionic-type reactions and reaction-retention times have not been investigated fully. Although iron (II) begins to precipitate in the same pH region as iron (III), the solubility of its hydrated oxides is such that the desired low residual iron levels are not attained until the pH ranges between 8.5 and 9.5. Aluminum removal from mine drainage has received little attention perhaps since its precipitation tends to coincide with iron. Aluminum (III) concentrations in these waters vary widely ranging from traces to levels substantially in excess of the iron. Literature is voluminous in the area of solubilization of aluminum-bearing clays and materials by sulfuric acid. Aluminum (III) begins to precipitate as the hydrous oxide in the 4.5 pH range and reaches minimal solubility about pH 6.0 to yield residual concentrations less than 1 mg/litre. Further increases in pH will result in an enhanced solubility due to its amphoteric nature.

The sulfate level in the sludge is variable as its degree of removal from the drainage waters tends to be limited. Apparently, most of the sulfate remains soluble in the water as a permanent hardness. However, in drainage waters whose level of acidity reauires the addition of concentrations of calcium reagents which exceed the solubility level of calcium sulfate (0.298 gm/100 ml. in cold water), this compound will precipitate and change sludge properties.

Process parameters include the order of unit operations, reaction rates, completeness of the reactions, temperatures, agitation, catalytic effects and bacteriological influences. Sludges prepared during treatment and the naturally-occurring sludges also differ. Materials within this latter grouping have not been characterized in detail. Bacteriological effects on sludge properties, especially related to the oxidation of iron (II) to iron (III) by autotrophic species in acid systems have been noted in the copper and uranium industries.

The composition of two sludges from drainage waters are listed below. In one case the raw water ranged between 200 - 700 ppm acidity and 70 - 195 ppm iron and was treated with hydrated lime (lc), while the other was from waters ranging from 1000 - 3000 ppm acidity and 400 - 1200 ppm iron (lb.).

Mine Water Sludge Composition

Component	Weight Percent (1c)	Weight Percent (1b)
$CaSO_4$	40	
$MgSO_4$	5	
CaO	3	
MgO	1	
Fe_2O_3	15	
Mn_2O_3	4	
SiO_2	20	
Al_2O_3	12	
SO_4^{-2}		29.4
Mg^{+2}		0.2
Ca^{+2}		12.0
Fe^{+3}		19.2
Al^{+3}		4.0
CO_3^{-2}		3.9
H_2O		19.6
Insolubles		0.5

Physical Properties of Mine Drainage Sludge

Sludge settling behaviour is difficult to adequately describe. The term "sludge settleability" has been used to relate the combined response of settling rate and final sludge volume. One researcher related the sludge settleability with respect to reagent (descending order): Na_2CO_3, $CaCO_3$, NaOH, CaO and $Ca(OH)_2$. An extensive study of sludge settling rates, densities and compaction levels as a function of neutralization reagents determined with synthetic drainage solutions reports sedimentation velocities up to 2.08 and compression velocities up to 0.086 inches/minute for Na_2CO_3. It appears that carbonates yield a more granular, dense sludge in comparison to the gelatinous, voluminous flocs resulting from the hydroxides. Thus, limestone sludge appears to have the highest settling rate followed by sodium carbonate, milk of lime and caustic soda. A drainage water in which the iron is all ferric and neutralized with lime to a pH of above 6 tends to yield a sludge which settles with a clearly defined interface and a clear supernatant. If some ferrous species remain, the pH is not quite proper, or the reactions are incomplete, the supernatant tends to remain cloudy, as the system is in a state of change. When limestone is employed, the long range settling rate may be more rapid and the sludge becomes more dense and compacted yet the intermediate settling may be slower possibly discharging turbid waters.

Sludge volume as achieved in a settling pond has been reported to approximate that of 1/3 of the water treated but to compact to a final volume of three percent after transfer to a secondary storage basin for extended periods. This latter product achieved a density of 13.9 percent solids by weight. Sludge compaction levels in a pond have been reported to reach five or six percent by weight after several days. At these levels the sludge is readily pumpable and transportable by tank truck. Other operators indicate that sludge consistency commonly will not exceed the one percent level. Pilot data on various waters indicated clarifier underflow could vary between 0.9 and 4.98 percent when employing hydrated lime solution. Sludges resulting from limestone precipitation generally settle to a "rather dense mass". This density may be enhanced by the presence of unreacted limestone fines and possibly the presence of iron carbonate species. Increased sludge density and the dewatering ease of limestone sludges have been reported and related to solution pH at time of precipitation. Ranges between 6.0 - 7.5 pH were presumed best. Design tests indicate such a sludge to occupy only one-fourth the volume of that resulting from hydrate lime neutralization. Limestone sludge volumes have been reported at one percent of treated water volumes with the sludge having 12 percent solids by weight in comparison with lime sludges having volumes of ten percent whose solids contents were 1.2 percent by weight.

Sludges formed during the oxidation of iron (II) to (III) which are bacteriologically active tend to be relatively more dense, less hydrated and somewhat "sticky" and cohesive in nature. This active sludge has a bright orange-brown colour at temperatures of 15 to 20°C, but darkens as the temperature is lowered towards zero. This sludge is reported to settle at a rate of several feet per hour.

Various procedures have been proposed to enhance sludge density and reduce its volume. Recycling, a concept which has been helpfully employed in the treatment of domestic sewage for some years, offers promise.

From: Neutralization of Acid Mine Drainage by D. W. Hill, Journal WPCF, Vol. 41, No. 10, October, 1969.

At the present time there is no generally applicable theory which can be applied to predict the nature or behaviour of precipitate formed from the many complex solutions encountered in the field of acid mine drainage. Until the time when such theory is developed, each drainage stream will have to be considered and tested as a unique waste. This fact must be kept in mind to achieve maximum efficiency in any new acid mine drainage treatment plant at a new site. Any plant design intended to treat acid mine drainage at several locations must provide great flexibility in operation, particularly if locally available limestone is to be used for neutralization. Sludge recycle may be desirable in some cases and not in others; two-step neutralization may be required in some areas; one-step neutralization with limestone may be sufficient in a few locations; while other locations may require that only slaked lime be used.

In any case, when locally available limestone is intended for use, an economic evaluation must be made to balance the cost of materials including the alternative of the cost of slaked lime against treatment efficiencies and effluent qualities. The very turbid and persistent suspensions produced by artificial dolomitic limestone suggest that a very critical view be taken in any situation where dolomitic limestone alone is recommended for neutralization, particularly if a clear effluent is expected.

In addition to effluent clarity, sludge characteristics are an important consideration in selecting a neutralizing agent. If sludge handling problems are significant, the more compact limestone-produced sludge may be preferred. However, if a sludge with flocculating properties is desired within the treatment process, slaked lime-produced sludge may be a requirement.

Several experimental results suggest that neutralization is more efficient and sludge flocculation is improved by treating more concentrated solutions. This observation suggests that care should be taken, where appropriate, to insure that the influent to the plant is not diluted prior to treatment by any water that does not itself need treatment.

For dilute acid drainage, consideration well might be given to a two-process treatment using ion exchange, reverse osmosis, or electrodialysis for the initial, more dilute drainage and neutralization for the more concentrated waste produced. Of course, treatment must be geared to the intended use of the treated water.

Attempts at sludge recycle and observations of settling times and sludge characteristics suggest that the value of sludge recycle is questionable. A small advantage might be the production of a more concentrated solution in which neutralization is more efficient.

Disposal of Sludges

The disposal of neutralization plant sludges is not yet a major problem in the hardrock mining districts of Ontario. However, as treatment plants become smaller, more mechanized and more efficient, the proper disposal of sludges will become very important.

In most cases, sludges should be returned underground. That is, either the dry 'cake' or watery suspension that constitutes the sludge should be returned to an abandoned section of the mine where it originated or, at least, should be directed to abandoned mine workings in the vicinity.

Sludges can, of course, be stored on the surface in impermeable impoundment areas. These areas, however, are in direct contact with the atmosphere. The combined effects of precipitation, sun, wind and fluctuating temperatures may have undesirable effects. Sludges do not dry easily and abnormal periods of precipitation may result in contaminated runoff from the storage area. In Ontario, on a yearly basis, the amount of evaporation does not generally surpass the amount of precipitation.

It has been suggested that sludge could be mixed with an appropriate amount of earth and then treated as sanitary landfill. From an environmental standpoint, this is probably not a good practice.

Sludge can be recycled from a treatment facility to the tailings impoundment area. Before this is done, however, the chemical stability of the sludge itself under the varying conditions of the tailings area should be thoroughly investigated.

References used in this section:

"An Experimental Investigation of the Treatment of Acid Mine Water Containing High Concentrations of Ferrous Iron with Limestone" by Holland, Berkshire and Golden, West Virginia University, Morgantown, W. Va.

"Neutralization of High Ferric Iron Acid Mine Drainage" by Wilmoth and Scott, U.S. Dept. of the Interior, Federal Water Pollution Control Administration, Norton Mine Drainage Treatment Laboratory, Box 60, Norton, West Virginia 26285.

"Mining Chemicals Handbook - Mineral Dressing Notes No. 26" by American Cyanamid Company, Wayne, New Jersey 07470.

OPTIMUM pH FOR THE PRECIPITATION OF METALS CONTAINED IN ACID MINE DRAINAGE TYPE EFFLUENTS

The overall solubility of Fe^{+2} and Fe^{+3} in mine water is determined by many factors, none of which can be evaluated as an isolated variable. However, for both Fe^{+2} and Fe^{+3} the limiting solubility at any pH is the solubility satisfying the equations:

$$K_{sol}\ Fe(OH)_2 = \left[Fe^{+2}\right]\left[(OH)^-\right]^2$$

and

$$K_{sol}\ Fe(OH)_3 = \left[Fe^{+3}\right]\left[(OH)^-\right]^3$$

therefore:

Solubility of $Fe(OH)_2$ and $Fe(OH)_3$ from K_{sol} at 25°C

$K_{sol}\ Fe(OH)_2 = 5.25 \times 10^{-14}$

$K_{sol}\ Fe(OH)_3 = 1 \times 10^{-38}$ (also 10^{-40} is reported)

pH	Fe^{+2}, ppm	Fe^{+3}, ppm
1		56,000
2		560
3		0.56
4		0.00056
5		
6	29,400	
7	294	
8	2.94	
9	0.0294	

Ferrous Iron

Equilibrium composition for the system Fe^{+2} - $Fe(OH)_2$ at various pH values expressed as a faction of the total Fe^{+2} present.

pH	5.0	6.0	6.5	7.0	7.5	8.0	9.0
Fe^{+2}	0.999	0.903	0.485	0.087	0.0094	0.00095	0.00001

Ferric Iron

Equilibrium composition for the system Fe^{+3} - $Fe(OH)_3$ at various pH values expressed as a faction of the total Fe^{+3} present.

pH	1.00	1.25	1.50	1.75	2.00	3.00
Fe^{+3}	0.8677	0.1947	0.0979	0.0213	0.0085	0.000008

The distribution of Fe^{+2} and $Fe(OH)_2$ as a function of pH is graphically illustrated in Figure 1. Similarly, the distribution of Fe^{+3} and $Fe(OH)_3$ as a function of pH is illustrated in Figure 2.

FIGURE I. DISTRIBUTION OF Fe^{+2} AND $Fe(OH)_2$ AS A FUNCTION OF pH

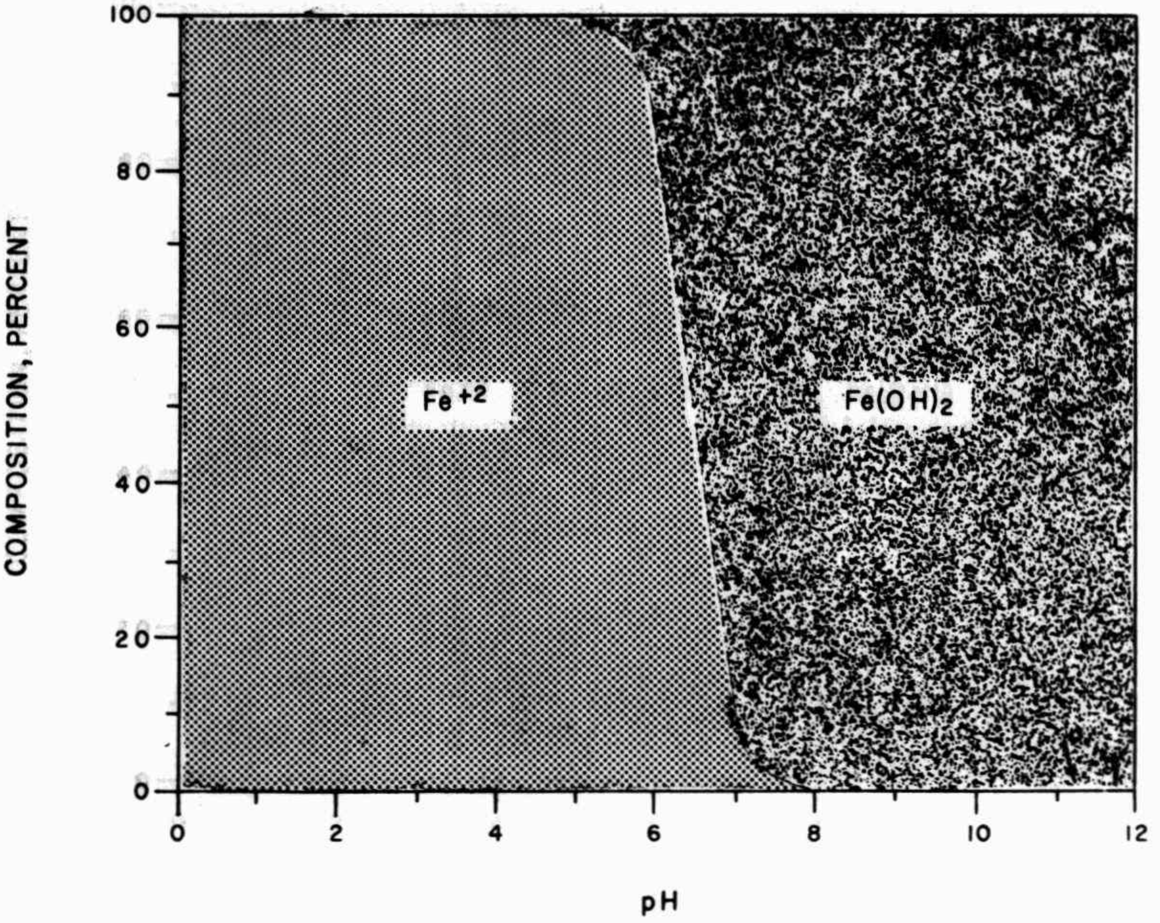


FIGURE 2 DISTRIBUTION OF Fe^{+3} AND $Fe(OH)_3$ AS A FUNCTION OF pH

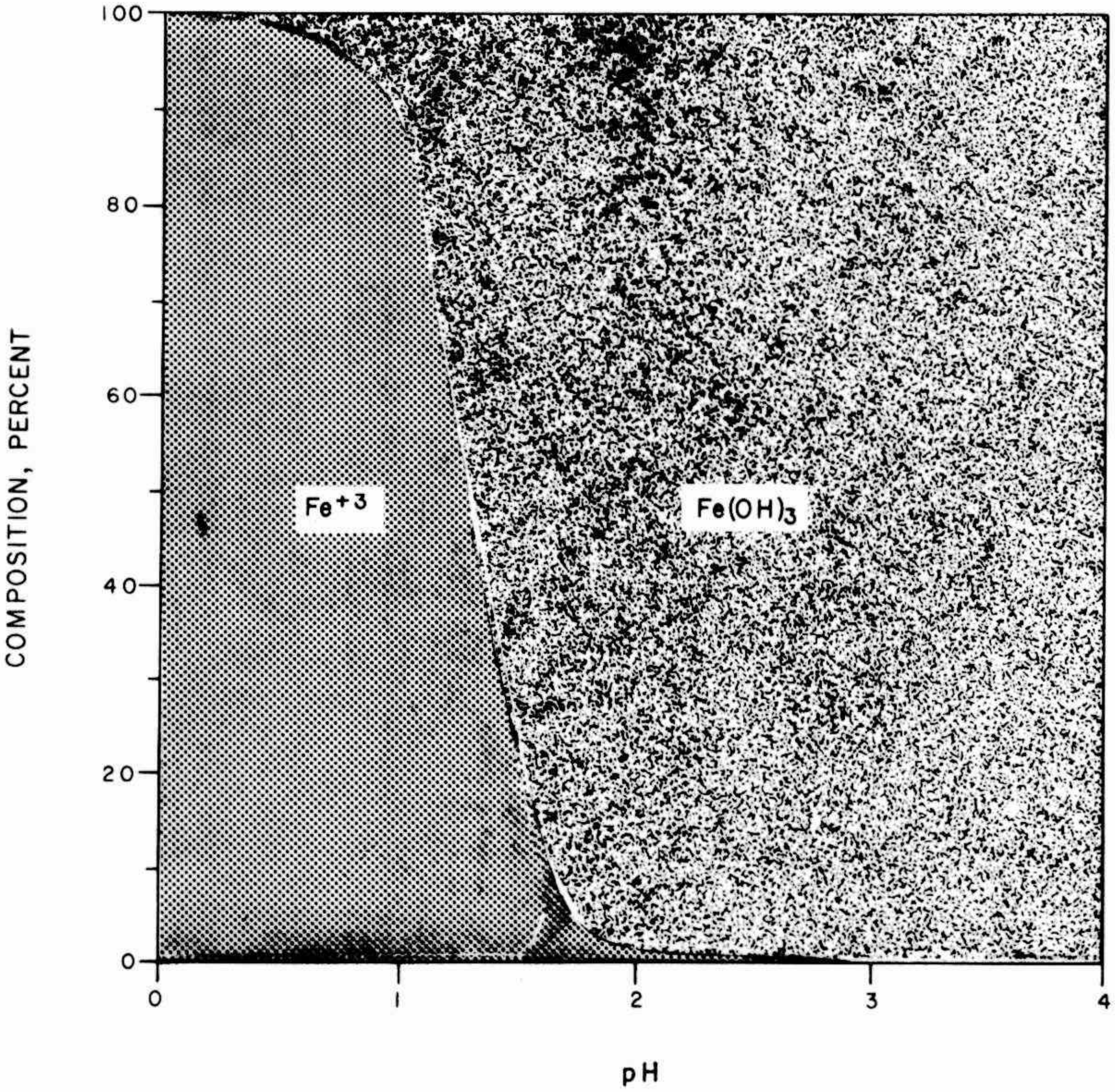


Figure 2 indicates that the ferric ion cannot exist, as such, in a solution having a pH much greater than 3.0. It must revert to a hydroxide-type form. Limited amounts of ferrous ion, however, can exist in solution at a pH of 8.0 (as indicated by Figure 1). If a decant is maintained at a pH of 5.0 ferric iron in the overflow will be largely in the form of the relatively harmless hydroxide. However, it is possible that small quantities of ferrous ion will also exist in the overflow and hence leave the tailings area. If the ferrous ion is associated with the sulphate ion (as it usually is), then downstream oxidation will give rise to ferric sulphate that will hydrolyze to form ferric hydroxide and sulphuric acid. The probable result would then be a downstream pH depression. The downstream pH depression, of course, would create conditions whereby the ferrous ion could migrate even farther downstream and so on until a natural balance between the amount of acid being produced and the alkaline characteristics of the downstream environment was reached.

At a pH of 8.0 (necessary to meet the requirements of iron), many metals do not precipitate to the extent that the resulting effluent can meet water quality standards. At a pH of 8.5, however, most problems are overcome. If undesirable quantities of specific metals (Zn, Ni, Mn, etc.)

still remain in the effluent, the pH should be further increased. If a pH increase is impractical or ineffective, another waste treatment method should be implemented.

Figures 1 and 2 indicate that at pH values less than 3.0 significant quantities of both ferrous and ferric iron can co-exist in solution and hence the acid mine drainage process becomes very efficient. Masses of hydroxides do not clog up oxidation sites or block solution passageways. Unfortunately, as the pH drops below 3.0, ideal conditions are set up for a bacterial attack on the sulphides. Once this attack is firmly established, the acid mine drainage process is practically irreversible.

Reference for this section: "Status of Mine Drainage Technology" by E. A. Zawadzki, July 1967, Bituminous Coal Research, Inc., 350 Hochberg Road, Monroeville, Pennsylvania.

THE COLLECTION OF EFFLUENTS

All effluents from a specific property should be diverted to a common point for treatment before discharge to a watercourse.

Quite commonly, an acid mine drainage problem at a specific property is magnified in the eyes of the public by the simple fact that wastes are discharged not to one watercourse but to several. Most operations, of course, utilize one or more decant structures that discharge to a common depression, stream, or lake. However, what has been forgotten is that seepage flows which are generally low-volume highly-contaminated untreated flows, discharge from the base of almost every dam on the property. One or more of these flows will probably discharge into a stream or lake that is not related to the watercourse receiving the decant overflow. The result is the potential for impairment of two or more watercourses instead of one. Furthermore, two or more treatment systems would be required instead of one.

WASTEWATER RECYCLE

Acid mine drainage is more than just a problem of specific contaminants. It is a problem of volume. If the overall water requirement of any specific mine-mill operation can be reduced, the problem of subsequent waste treatment becomes smaller.

The most effective way to minimize an overall acid mine drainage problem during the years of conventional mine-mill operation is to reduce the total volume of effluent that leaves the property. The most convenient way to reduce the total volume of effluent leaving the property is to set up the mine-mill complex on the basis of maximum possible water re-use.

Total wastewater recirculation in the sulphide mining industry is not easy to attain. Some of the reasons for this are as follows:

(1) Sulphide flotation circuits are somewhat sensitive to major changes in water quality. If a sulphide mill is put in closed circuit with a tailings area, traces of persistent flotation reagents can be taken into the mill via the wastewater return line. Loss of flotation control is possible. This problem can generally be countered, however, by reducing the addition rates of specific persistent reagents to the mill circuit. In this manner total reagent costs can be reduced. Also a reduction in the waste loadings from the property can result since reagent consumption has been reduced (in other words the reagents are being used more efficiently).

Similarly, the re-use of underground (or open pit) mine water in a mill that employs normal froth flotation circuits can cause problems if the water contains significant quantities of organic materials such as oil. The occurrence of trace quantities of oily materials in underground mine water as a result of mining operations is not only possible but is probable.

Abnormal quantities of soluble and suspended materials introduced into the mill via the wastewater return line have the potential ability to adversely affect basic operations such as ion exchange, thickening, filtration, precipitation and pH control.

(2) The successful operation of a total wastewater recirculation system is difficult since a complete water balance must be maintained at all times within the mine-mill complex. Water imbalances, however, are probable and can result as follows:

(a) Mine Water

Mine water is simply water that has been pumped from the underground workings of a mine to the surface for disposal (Note: water that is pumped from open pit workings is also referred to as mine water). A limited amount of water is actually directed underground from the surface for various industrial purposes (i.e., for use as cooling water, dust control, etc.).

In most cases, an underground mine acts in much the same manner as a well that is used as a source of drinking water. As a result of faulting, etc., coupled on occasion with diverse solution effects, very sophisticated natural drainage networks can be set up within a particular ore deposit. When the mine workings intersect these natural water-carrying channels, water flows into the mine. Depending, therefore, on the geology of the situation, some mines are very 'wet' (they 'make' water) and some mines are relatively 'dry'. In most cases, however, an underground mine will 'make' considerably more water than is required for normal underground operations. For instance, a large active mine in many instances will collect thousands of gallons of 'unwanted' water each day. This water is generally contaminated and should be chemically and/or physically treated before it is discharged to a natural watercourse.

Water in a mine generally flows to one or more sumps (collection basins). Depending on the volume of water to be handled, the water is pumped to the surface on an intermittent or continuous basis. If this excess mine water is directed to a mill that is in closed circuit with its own tailings area, a water imbalance results that in turn, generates a decant flow from the tailings area.

There are many reasons why excess mine water should be directed to a mill complex for re-use if at all possible. However, if the mill in question is operating or is to operate in closed circuit with its own tailings area, excess mine water should not enter the mill recycle system at any point unless the recycle system requires continuous or periodic additions of make-up water. There are specific sulphide flotation circuits that apparently require fresh make-up water. However, if this requirement is not valid, then excess mine water can be used.

(b) Atmospheric Water

Natural precipitation (rain, snow, etc.) falling on a tailings area frequently creates a significant oversupply of water as far as recirculation from a tailings area decant to a mill is concerned. In the sulphide mining district of Ontario, natural precipitation can theoretically account for up to 2,000 imperial gallons of seepage (or excess water) per acre per day.

All reasonable efforts, of course, should be made to divert streams and large springs around a tailings area or away from a tailings area.

In view of all of the above, it becomes obvious that total wastewater recycle in a mine-mill complex is often impossible to achieve. However, partial recycle is possible in nearly every case. In cases where total recycle cannot be achieved, a continuous or periodic decant flow will be generated. If the environment is to be protected, the decant flow must be chemically and/or physically treated before it can be released to a watercourse.

When a mine-mill complex is being designed on a recycle basis, strict attention should be paid to the industrial uses of all recycle streams. For instance, if backfill is not being used in a mine, the chemical composition of the mine wastewater may be radically different from the composition of the mill wastewater. As a result, the waste treatment requirements of the mine and mill wastewaters may differ significantly. A troublesome contaminant that originates in the mill may not appear at all in the mine water or may appear in the mine water in greatly reduced quantities. In cases of this nature, a separate treatment system for mine water could conceivably result in savings in the overall cost of waste treatment. If backfill is being used in a mine, mill water will generally be used to repulp the coarse tails that are being sent underground. Hence, mill contaminants end up in the mine water. This is almost always the case but, if convenient, the concentrations of mill contaminants in the mine water can be minimized by using mine water itself to repulp the tails.

Water is also 'lost' in a sulphide mine-mill wastewater recycle system. These losses are usually welcome since unwanted water tends to plague the operator of a recycle system.

Water losses occur as follows:

(1) sulphide concentrates (i.e., the product of the mine-mill operation) are generally shipped as a 'cake' that contains up to 15 percent water.

(2) drying operations that may be associated with mine-mill circuits drive off water as steam or vapour.

(3) some significant evaporation does occur on a tailings area during the warm summer months. However, evaporation effects should be ignored when a recycle system is being designed for an Ontario plant location.

(4) after settling in the impoundment area, the tailings will be associated with some residual moisture. In some cases, the settled tailings will contain up to 25 percent (by weight) of residual moisture.

In the sulphide mining industry, wastewater recycle:

(a) significantly reduces the volume of fresh water that is required daily to sustain processing operations.

(b) significantly reduces the total volume of wastewater that is discharged to the environment.

(c) reduces waste loadings from a property since reagent additions in the mill will, in all probability, be reduced. Also, precipitation, coagulation and settling effects in the tailings area, on a recycle basis, will tend to reduce overall waste loadings.

(d) reduces the required size of all waste treatment units due to the lower volume of all waste flows. Also, recycle permits the installation, if necessary, of very efficient and specific waste treatment units that are generally not available in sizes that are able to handle very large volume waste flows.

GANGUE SULPHIDE REMOVAL

$$2FeS_2 + 2H_2O + 7O_2 \dashrightarrow 2FeSO_4 + 2H_2SO_4$$

In a simple sense, the above chemical equation describes the role of the iron sulphide minerals in an acid mine drainage situation.

Iron sulphide minerals (pyrite, pyrrhotite and marcasite) are generally treated as waste products in milling circuits where valuable 'ore' sulphides are being recovered. The iron sulphide minerals, in a finely divided state and intimately mixed with significant quantities of other gangue (waste) material, are discharged to an engineered or natural impoundment basin which is referred to as a 'tailings area'. Here, under appropriate conditions, the iron sulphide minerals spontaneously decompose into water soluble salts and acid.

The reaction products of the iron sulphide minerals are directly responsible for the following problems in Ontario hardrock sulphide camps:

(1) They contaminate most aqueous flows that originate at or come into contact with a sulphide mining property. In most cases, the contaminating substances can be removed from the flows only with difficulty. As a result, extensive and expensive chemical and physical waste treatment units are generally required.

(2) Because the iron sulphide reactions are of a spontaneous

nature, serious environmental problems can occur at a property for years and even decades after the property has been abandoned. In all cases, however, waste treatment must continue. This, of course, is an extremely serious situation for a small "one mine" company. It is possible that all the profits from a small successful mining operation could be consumed by post-operation waste treatment. However, the situation for a large company that controls many mining operations is even more serious. As one mine after another closes down, the cumulative cost for post-operational waste treatment could be devastating. Some large companies in the Province of Ontario are just beginning to appreciate this fact.

(3) They create a severe chemical environment within a tailings mass. Normally non-reactive minerals acquire varying degrees of reactivity and, as a consequence, the complexity and magnitude of the contaminant load from the area is increased.

(4) They create and maintain conditions upon and within a tailings area that are definitely toxic to most forms of vegetation.

IF A TAILINGS AREA IS SULPHIDE FREE, ACID MINE DRAINAGE WILL NOT BE GENERATED.

The most effective way to prevent an acid mine drainage situation from arising at any particular property is to separate all gangue sulphides (pyrite, pyrrhotite, marcasite, etc.) from all non-sulphide gangue (silicates, oxides, carbonates, etc.) in the milling circuit itself (or at least prior to discharge to a common tailings area) and to discharge each gangue fraction (sulphide and non-sulphide) to a separate tailings area. The required gangue sulphide-non-sulphide separation can be accomplished with a degree of ease in present milling circuits using conventional equipment. In fact, a gangue sulphide-ore sulphide separation is, at present, made in many of the milling circuits in the Province. However, at the present time, the gangue sulphides (iron sulphides) are generally depressed into the non-sulphide gangue in the mill and, as such, are sent to a common tailings area as an intimate mix with non-sulphide gangue.

"Bulk floats" are also relatively common in the sulphide mills of the Province. A "bulk float" is a straight sulphide-non-sulphide separation. The sulphide fraction of the float is composed of both ore sulphides and gangue sulphides.

Gangue sulphide separations can be made in many ways in a sulphide milling circuit. The method that is best for any particular ore must be chosen by mill personnel since many complicating factors can arise. Mill personnel must also choose the point in the circuit at which sulphide recovery is realized.

Although the mill discharge (i.e., the influent to the tailings area) may appear to be the most promising point at which gangue sulphide (plus residual ore sulphide) recovery could be attempted (probably using "bulk float" technology) this may not be so in a few cases. Reactive iron sulphide particles, during their passage through an extensive milling circuit, could conceivably aquire surface coatings of molecular thickness which could reduce the overall efficiency of a float.

It is important to realize that the primary purpose of conducting a gangue sulphide float is to prevent gangue sulphides, in any significant quantity, from reaching a particular tailings area that has been set aside to receive non-sulphide tailings only. In this context, it is necessary to emphasize two very important facts:

(1) Flotation technology has not developed to the stage where 100 percent efficiency has been achieved. However, efficiencies in the order of 97 percent are becoming common.

(2) Tailings areas that are well known as acid producers in the Province of Ontario have iron sulphide contents ranging from 2.5 percent to 72 percent. It is suspected that acid mine drainage conditions will occur even when the iron sulphide

content of a tailings mass is less than 2.5 percent.

Therefore, in order to prevent an acid mine drainage situation from developing in any particular tailings area, the (iron) sulphide content of the mass must be kept substantially below 2.5 percent and probably as much below 1 percent as possible.

Gangue sulphide recovery should begin the moment a sulphide operation comes into production and should remain as an integral part of the mine-mill circuit for the entire life of the property.

Sulphide properties that are already in production should add gangue sulphide recovery systems to their circuits if at all possible. This would permit each mill to deposit a layer of non-pyritic tailings over existing masses of pyritic tailings and, as a result, would facilitate revegetation of the tailings areas.

THE DISPOSAL OF GANGUE SULPHIDE CONCENTRATES

The disposal of gangue sulphide concentrates is a problem that is generally vastly overrated.

Two important relevant facts must be noted:

(1) The gangue sulphide content of different sulphide orebodies varies greatly (from less than 1 percent to greater than 60 percent). Therefore, the magnitude of the problem of the disposal of gangue sulphide concentrates will also vary from property to property.

(2) The specific gravities of the iron sulphide minerals are as follows:

Mineral	Specific Gravity
Pyrite	5.013 to 5.018
Marcasite	4.887
Pyrrhotite	4.58 to 4.65

The average specific gravity of the non-sulphide gangue may be roughly estimated by the following:

Mineral	Specific Gravity
quartz	2.65
feldspar	2.55 to 2.76
mica	2.8 to 3.4

In general, therefore, the specific gravity of the sulphide gangue is roughly twice that of the non-sulphide gangue. As a result, sulphide gangue concentrate will occupy significantly less space (approximately one half) than an equivalent weight of non-sulphide gangue (bulk density is a very important factor here).

The above two facts are applied in the following manner:

Case #1

Surface area of completely filled tailings basin -- 100 acres

Average depth of tailings -- 10 feet

Pyrite (gangue sulphide) content of tailings -- 3 percent (by weight)

If gangue sulphide recovery had been initiated when production commenced at this property, the gangue sulphide concentrate could have been stored in a natural or engineered impoundment basin having a total surface area of less than 2 acres (10 foot depth) or 1 acre (20 foot depth). The main impoundment area (for non-sulphide gangue) would have remained at 100 acres).

Case #2

Surface area of completely filled tailings basin -- 100 acres

Average depth of tails - 10 feet

Pyrite (gangue sulphide) content of tailings -- 30 percent (by weight)

In this particular case, the gangue sulphide concentrate could have been stored in a separate impoundment basin having a total surface area of 15 to 20 acres (10 foot depth) or 7½ to 10 acres (20 foot depth). The main non-sulphide area would perhaps occupy 85 acres.

Case #3

Surface area of completely filled tailings basin -- 100 acres

Average depth of tails -- 10 feet

Pyrite (gangue sulphide) content of tails -- 60 percent (by weight)

In this case, 30 acres (10 foot depth) or 15 acres (20 foot depth) would be required for gangue sulphide storage. The main (non-sulphide) area would thereby be reduced to 60 or 70 acres in extent.

In all cases, it is preferable but not necessary that the gangue sulphide and non-sulphide gangue storage areas exist as separate entities. If separate areas cannot be found for storage, a single two-compartment basin can be constructed. If two separate areas are to be constructed, they should be as close to each other as possible in order to avoid possible duplication of waste treatment facilities.

Referring to the gangue sulphide storage area itself:

(1) In order to prevent seepage flows, all man-made dams that serve to enclose the basin must be impermeable. In this sense, therefore, the basin should be contained, as

much as possible, by natural impermeable contours.

(2) The deepest basin available for storage should be chosen. In this way, the surface area of the basin will be kept to a minimum and, as a result, the ensuring effects of runoff will be minimized.

(3) If revegetation of the gangue storage area is required, this can be accomplished by spreading a layer of coarse waste rock (or coarse gravel) over the entire surface of the area and then spreading over this a layer of any available soil that will support growth. The layer of coarse waste rock acts to prevent the migration of toxic ions from the gangue sulphide concentrate into the soil layer.

(4) The overflow from an active basin that is being used for gangue sulphide storage should be directed in such a manner that it eventually passes through a waste treatment unit. The main waste treatment unit for a property should always be associated with the non-sulphide gangue storage area since this area, in most cases, is relatively large, contains residual sulphide concentrations, may be a major source of seepage and, in general, will receive the largest volume of wastewater from the mill.

THE ECONOMIC JUSTIFICATION FOR GANGUE SULPHIDE REMOVAL

An economic justification for gangue sulphide removal at a mining property generally cannot be based on the value of the concentrate produced.

In nearly every case, the gangue sulphide concentrate produced would consist almost entirely of various iron sulphide minerals. Iron sulphide can be used for the production of sulphuric acid and as a source of iron. However, at the present time, there is an abundance of good quality iron ore and an oversupply of sulphuric acid. This situation will not change quickly. Iron sulphide minerals do, on rare occasions, contain significant quantities of desirable substances (for example, tin) and, as a result, an incentive is provided for gangue sulphide recovery. The extractive metallurgy, however, in such cases is usually difficult.

In order to realistically evaluate the effectiveness and cost of most waste treatment systems, it is necessary to assume that the substances removed from the waste streams have no monetary value. The concentrate that would be produced as a result of a gangue sulphide recovery system is no exception.

Tailings areas that do not contain iron sulphide minerals (sulphides in general) do not give rise to acid mine drainage flows and, as a result, the type of waste treatment that is necessary in an acid mine drainage situation need not be applied. On the other hand, tailings areas that do contain iron sulphide minerals (sulphides in general) will, with a few exceptions, generate acid mine drainage flows. Extensive and long-term treatment facilities are required. It is on this basis that an economic justification for gangue sulphide removal can be made.

Many sulphide mining properties in the Province of Ontario are experiencing problems due to acid mine drainage. In most cases, chemical waste treatment facilities have been installed and serve to counter the problem. In these cases (and there are many), the initial cost of the waste treatment plant is known as is the daily operating cost (power, bulk reagents, etc.) of the plant. Since almost all of the iron in the flows that are being treated is derived from the decomposition of the iron sulphide minerals in the tailings mass and since the total amount of iron that is being discharged in the (seepage) flows each day is known, the total length of time that chemical waste treatment will be required at any particular property can be roughly calculated. In the average situation, chemical treatment will be required for decades after milling ceases. Compare the total cost of chemical waste treatment over the total time indicated with the total expected cost of gangue sulphide removal during the operating life of the mine-mill complex. In most cases, it will be readily apparent that the gangue sulphide recovery route is, by far, the most economical route. Moreover, from an environmental standpoint, gangue sulphide recovery is the most acceptable route since significant waste treatment is accomplished with only negligible (flotation) reagent additions. The chemical waste treatment route involves massive reagent additions (lime, etc.) which, in turn, may cause environmental problems of their own (i.e., increase in total dissolved solids, increase in calcium, etc.).

The potential waste treatment costs arising from acid mine drainage generation at any particular sulphide property can be calculated as shown in the following example:

Type of sulphide operation -- copper, lead, zinc

Planned Production -- 3,000 tons/day

Gangue (iron) sulphide content of ore -- 40 percent (by weight)

Expected life of mine -- 5,000 working days

(refer to section entitled "The Chemistry of Acid Mine Drainage")

Equation #1

$$\underset{239.950}{2FeS_2} + 2H_2O + 7O_2 \longrightarrow \underset{303.817}{2FeSO_4} + \underset{196.155}{2H_2SO_4}$$

In this equation

1 lb. of FeS_2 is required to produce (a) 1.27 lbs of $FeSO_4$

(b) .82 lbs of H_2SO_4

Equation #2

$$4FeSO_4 + 2H_2SO_4 + O_2 \text{ ------}\!> 2Fe_2(SO_4)_3 + 2H_2O$$

607.634 196.155 799.758

In this equation

1 lb. of $FeSO_4$ is required to produce 1.32 lbs of $Fe_2(SO_4)_3$ and 1 lb. of H_2SO_4 is required to produce 4.08 lbs of $Fe_2(SO_4)_3$

Equation #3

$$Fe_2(SO_4)_3 + 6H_2O \text{ -----}\!> Fe(OH)_3 + 3H_2SO_4$$

399.880 294.234

In this equation

1 lb. of $Fe_2(SO_4)_3$ is required to produce .74 lbs of H_2SO_4

Often, the three equations above are added, giving the overall stochiometric relationship:

$$FeS_2 + \frac{15}{4} O_2 + \frac{14}{4} H_2O \text{ -----}\!> 2H_2SO_4 + Fe(OH)_3$$

119.975 196.155 106.869

Therefore, under more or less perfect conditions, 1 lb. of FeS_2 (pyrite) will produce 1.6 lbs. of sulphuric acid.

In the example (an actual case) given at the beginning of this section, the mine-mill operation is discharging 1,200 tons per day of iron sulphide gangue to the tailings area. When operations are suspended at this property (after 5,000 working days), the tailings area will contain 6,000,000 tons of iron sulphide gangue.

Since 1 lb. of iron sulphide gangue has the capacity to spontaneously form 1.6 lbs. of sulphuric acid, the tailings area serving the property in question has the potential ability to release 9,600,000 tons of sulphuric acid to the immediate environment.

The potential waste treatment costs at this property can now be roughly evaluated since waste treatment will essentially revolve around the neutralization of 9,600,000 tons of sulphuric acid, the removal of entrained metals, and the subsequent disposal of all sludges.

NOTE: Most ores have at least a limited capacity for neutralization. This must be taken into account when calculating neutralizing reagent costs.

MINE-MILL REAGENT CHANGES

Acid mine drainage type effluents, especially from base metal mines, are toxic to many forms of animal and vegetable life. For instance, the many metals that form an inherent part of an acid mine drainage flow act in several ways to give rise to toxic environments. Salts of electropositive metals such as silver, molybdenum, antimony, thallium and tungsten react with proteins and destroy metabolites essential to vital function. Some metals pervade the active sites of an enzyme and render it useless through substitution for the normal metal constituents. These metals are selenium and tellurium and, to a much lesser extent, beryllium. Precipitation and chelation of essential metabolites is the mode of toxic action shown by aluminum, beryllium, scandium, titanium, yttrium, zirconium, barium and iron. Catalytic decomposition of proteins is shown by lanthanum and other rare earths. A final mode of toxic action is reaction with the cell membrane to alter its transport properties. Salts of gold, cadmium, copper, lead and uranium show this action.

pH, of course, plays a major role in increasing or decreasing the toxicity of specific substances. The permissible range of pH for fish depends on factors such as temperature, dissolved oxygen, prior acclimatization, and the content of various anions and cations. The pH determines the degree of dissociation of weak acids and bases, some of which may be more toxic in the molecular than the ionic form. For example, the toxicity of sodium sulphide to trout tends to increase with acidity as the pH changes from 9 to 6, i.e., as sulphide and HS^- ion are converted to H_2S.

The tolerance of fish to low concentrations of dissolved oxygen varies markedly with pH. The toxicity of nickel cyanide increases over 1000-fold as the pH of the solution decreases from 8.0 to 6.5. Fish that can tolerate pH values as low as 4.8 will die at pH 5.5 if the water simultaneously contains 0.9 mg/litre of iron.

Some of the minimum and maximum pH values, and recommended ranges in pH, as reported in various publications, are given in the following tabulation:

Limiting pH Values

Minimum	Maximum	Remarks
3.3	10.7	Trout survived without adverse effects
3.6	--	Tench survived two weeks but carp died
3.6	10.5	96-hour TLm range for bluegill sunfish
3.8	10.0	Fish eggs could be hatched, but abnormal young were produced at extreme pH's

Limiting pH Values

Minimum	Maximum	Remarks
4.0	10.0	The most resistant fish can tolerate such extreme pH values indefinitely after acclimatization
4.0	10.1	Limits for the most resistant species
4.0	10.4	Limits for bluegill sunfish with HCl and NaOH
4.1	8.5	Range tolerated by speckled trout in nature
4.1	9.5	Range tolerated by trout
4.3	--	Carp died in 5 days
4.4	8.7	Toxic limits for trout
4.5	8-9	Trout eggs and larvae develop normally
4.6	9.5	Toxic limits for perch
4.6	--	Tench died in two days
4.8	--	Lower limit for trout
4.8	--	Illness and early death for carp
4.8	9.2	Toxic limits for fish
5.0	--	Toxic limit for sticklebacks
5.0	9.0	Tolerable range for most fish
--	8.7	Upper limit for good fishing water
5.4	--	Lower limit for carp and tench

Limiting pH Values

Minimum	Maximum	Remarks
--	9.2	Upper limit for trout and perch
5.5	--	Lower limit for general fish protection
5.4	11.4	Fish avoided waters beyond these limits
6.0	11.0	Fish did not avoid waters in this range
6.0	7.2	Optimum range for fish eggs
6.5	8.4	Range tolerated by most freshwater fish

For other aquatic organisms, ranges were reported as follows:

Minimum	Maximum	Remarks
1.0	--	Mosquito larvae destroyed at this value
2.5	--	Tolerated by Chamydomonas, Fragilaria, Asterionella, Aphanizomenon
3.3	4.7	Mosquito larvae thrived in this range
4.0	--	Toxic for Paramecium, Volvox, Asplanchna
7.5	8.4	Good range for plankton production
--	8.5	Algae are destroyed above this value

Generally, it appears that most fish can tolerate extensive and rapid changes in pH (e.g., from 7.2 to 9.6 and from 8.1 to 6.0). It has been noted, however, that when the pH of a stream falls below 5.0 specialized flora and fauna develop. Some species have been observed at pH values as low as 2.9.

Add to all of the above, the toxic effects of a high total dissolved solids concentration and a high sulphate concentration and it is apparent that acid mine drainage flows will exert an adverse influence on the environment under almost all conditions.

One very important fact, however, should be kept in mind. Acid mine drainage flows in Ontario do not just reflect the results of naturally occurring chemical decomposition reactions that go on within a tailings mass or within a wastepile or within an orebody. In fact, at all active properties, the chemical characteristics of an acid mine drainage flow (particularly a tailings area decant) strongly reflect and are influenced by the chemistry of the mine-mill circuit itself. Many chemicals, of varying toxicity and persistence, are added to mine-mill streams in order to effect concentrate recovery. The toxicology of these materials must not be overlooked.

Lime (CaO), limestone ($CaCO_3$), sodium carbonate, ammonia and sulphuric acid all find wide use in the mining camps of Ontario. These substances are well-known. Less well-known, however, are the flotation reagents that find more or less common use in and associated with the sulphide flotation circuits of the Province. Chemicals that fall in this category include:

sodium diethyl-dithiophosphate

sodium diethyl and sodium disecondary butyl dithiophosphate

sodium diisopropyl dithiophosphate

sodium diamyl dithiophosphate

sodium sec-butyl xanthate

potassium ethyl xanthate

sodium ethyl xanthate

sodium isobutyl xanthate

sodium isopropyl xanthate

potassium amyl xanthate

potassium sec-amyl xanthate

potassium isopropyl xanthate

potassium hexyl xanthate

a series of fatty acid type products of vegetable origin [e.g., fatty acid content 92 percent (almost equal parts of oleic and linoleic acids), rosin acid content 4 percent]

another broad series that includes amines and amine salts; organic analogs of ammonium salts; organic sulphonium and phosphonium compounds in which sulphur or phosphorus has replaced the nitrogen atoms of the ammonium compound; and other materials which will ionize so that both the hydrocarbon and reactive groups of the promoter are part of the positively charged ion -- the cation.

anionic di(2-ethylhexyl) sodium sulphosuccinate
anionic n-octadecyl disodium sulphosuccinamate
cationic (mixture of the octadecyl amine and
    octadecyl guanidine salts of octadecyl
    carbamic acid reacted with ethylene oxide)
pine oil
cresylic acid
compounds of the formula $CH_3(O\ C_3H_6)_x\ OH$
creosote

Other materials commonly used in mine-mill circuits include:

sodium silicate
several phosphates including tetrasodium pyrophosphate and trisodium phosphate
acrylic polymers
copper sulphate
lead nitrate and/or lead acetate
sodium nitrate
sodium sulphide
sodium cyanide
sodium and calcium sulphites and hyposulphites

sodium hydrosulphite
zinc sulphate
chromate
permanganate
quebracho and tannic acids
starch, glue, gelatin
sodium hydroxide
sulphur dioxide
hydrofluoric acid
ferro and ferricyanides
etc.

Many of the above-mentioned compounds are very toxic. Others are less toxic. Some are persistent and hence will escape a tailings area. Others are unstable and will break down in a tailings area.

Obviously, when reagents are being chosen for a mine-mill circuit, the least toxic compounds should be chosen. Included in the definition of 'least' toxic compounds are those toxic compounds that break down rapidly (into innocuous substances) in a waste stream or those toxic substances which can be removed easily from a waste stream using recognized waste treatment technology.

In general, compounds having known or suspected nutrient properties should be avoided if possible.

Compounds that are persistent (that is, compounds that do not break down easily in a natural environment) should be avoided. Compounds that will act to significantly increase the total dissolved solids content of waste streams should be avoided. Compounds that act to increase the hardness (as $CaCO_3$) in a receiving stream should be avoided.

References for this section:

"Trace Minerals Affect Stream Ecology" by C. E. Lanford - The Oil and Gas Journal - March 31, 1969.

"Water Quality Criteria", Second Edition by McKee and Wolf, 1963, The Resources Agency of California, State Water Quality Control Board, Publication No. 3-A.

THE CONTAMINATION OF UNREQUIRED WATER RESOURCES

Unrequired water resources should never be needlessly contaminated.

Under no circumstances should fresh water be permitted to gain access to a sulphide-bearing tailings area. All reasonable efforts should be made to divert streams and large springs around a tailings area or away from a tailings area. Once in a tailings area, fresh water tends to pick up quantities of acid-producing water soluble salts, etc. The result is that chemical treatment is required for water that is not needed in the mine-mill process. The real significance of this factor is generally acknowledged only after the property has been abandoned and profit-consuming waste treatment facilities must continue to be operated.

Excess water on a tailings area, particularly an abandoned tailings area, helps to maintain undesirable seepage flows and may heighten problems of instability of embankment structures.

THE UTILIZATION OF NATURAL FORCES TO ACHIEVE A DEGREE OF WASTE TREATMENT IN ACID MINE DRAINAGE SITUATIONS

Characteristically, seepage flows that originate within a sulphidic tailings mass tend to change colour on standing while exposed to the atmosphere. Initially clear and colourless the waste assumes a faint yellow flush which, in time, gradually deepens to an intense amber-red. This latter colour is due to very finely divided suspended particles of hydrous ferric oxide ($Fe_2O_3.nH_2O$).

Ferrous iron is quite commonly found as a component of acid seepage flows and, in Ontario, occasionally represents over 50 percent of the iron species present. If a flow contains a relatively high ferrous to ferric ratio, we term the flow 'immature'. If the ferrous to ferric ratio is low, the flow is termed 'mature'. Obviously, as the ferrous iron in any flow oxidizes, the ferrous to ferric ratio decreases and the flow itself matures. Thus, highly coloured flows tend to be mature flows; colourless flows tend to be immature flows.

Fortunately the potential of the $Fe^{3+} - Fe^{2+}$ (ferric-ferrous) couple, 0.771 volts, is such that molecular oxygen can convert ferrous iron to ferric iron in acid solutions.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{3+} + H_2O$$

$$E^o = 0.46 \text{ volts}$$

In a basic solution, of course, the oxidation process is still more favourable:

$$\tfrac{1}{2}Fe_2O_3.3H_2O + e = Fe(OH)_2 + (OH)^-$$

$$E^o = -0.56 \text{ volts}$$

Neutral and acid solutions of ferrous iron oxidize less rapidly with increasing acidity (despite the fact that the potential of the oxidation reaction will become more positive).

The oxidation of ferrous to ferric species by molecular oxygen appears to involve the initial formation of an ion FeO_2^{2+}. The reaction kinetics also suggest that a binuclear species is a transient intermediate formed by the attack of Fe^{2+} on FeO_2^{2+}. The overall reaction of

$$FeO_2^{2+} + Fe(H_2O)^{2+} \dashrightarrow Fe(OOH)^{2+} + Fe(OH)^{2+}$$

leads to the hydroperoxo ion which rapidly decomposes to give Fe^{3+} and HO_2^-, which itself either oxidizes Fe^{2+} or decomposes to O_2.

One of the most conspicuous features of ferric iron (which all seepage flows of the type we are discussing contain) in aqueous solution is its tendency towards hydrolysis and/or formation of complexes. It has been established that the hydrolysis is governed in its initial stages by the following equilibria constants:

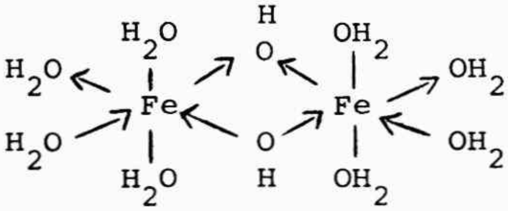
$$\left[Fe(H_2O)_6\right]^{3+} = \left[Fe(H_2O)_5\ (OH)\right]^{2+} + H^+ \quad K = 10^{-3.05}$$

$$\left[Fe(H_2O)_5\ (OH)\right]^{2+} = \left[Fe(H_2O)_4\ (OH)_2\right]^{+} + H^+ \quad K = 10^{-3.26}$$

$$2\left[Fe(H_2O)_6\right]^{3+} = \left[Fe(H_2O)_4\ (OH)_2Fe(H_2O)_4\right]^{4+} + 2H^+$$

$$K = 10^{-2.91}$$

In the last of the above equations, the binuclear species is written to imply the structure



which, though plausible, is quite unproved.

From the constants for these equilibria, it can be seen that even at the rather acid pH's of 2-3 (most acid seepage flows fall within or close to this range) the extent of hydrolysis is very great and, in fact, in order to have solutions containing ferric ion mainly (say approximately 99 percent) in the form of the pale purple hexaquo ion, the pH must be around zero. As the pH is raised above 2-3, more highly condensed species than the binuclear one noted above are formed. Attainment of equilibrium becomes sluggish and colloidal gels are formed. Ultimately, hydrous ferric oxide is precipitated. There is no evidence to suggest that any definite hydroxide, $Fe(OH)_3$ exists and the reddish-brown precipitate commonly called ferric hydroxide is best described as hydrous ferric oxide, $Fe_2O_3.nH_2O$.

The various hydroxo species, such as $[Fe(OH)(H_2O)_5]^{2+}$ are yellow in colour because of charge transfer bands in the ultraviolet which have tails coming into the visible. Thus aqueous solutions of ferric salts even with non-complexing anions are yellow unless extremely acid. As colloidal hydrous ferric oxide accumulates the colour of the 'solution' will change to amber-brown and, under unusual circumstances, to deep blood-red.

The fact that seepage waste does generally turn colour on standing and the fact that advanced inorganic chemistry texts indicate that favourable reactions can occur spontaneously gave rise to the speculation that one method of obtaining partial treatment of seepage waste involving essentially no reagent costs would be the simple ponding of such wastes. Practical field experience in the Province of Ontario has indeed indicated that ponding of acid seepage wastes accomplishes some degree of waste treatment.

The cost of lime that is required to effectively neutralize (to a pH of 8.5) most seepage flows is prohibitive. Most of the lime (or NaOH, etc.) in this type of reaction is consumed not in reactions with free acid but in reactions with soluble (metal) salts (see Figure 3). This is all very well as the metals have to be removed in order that water

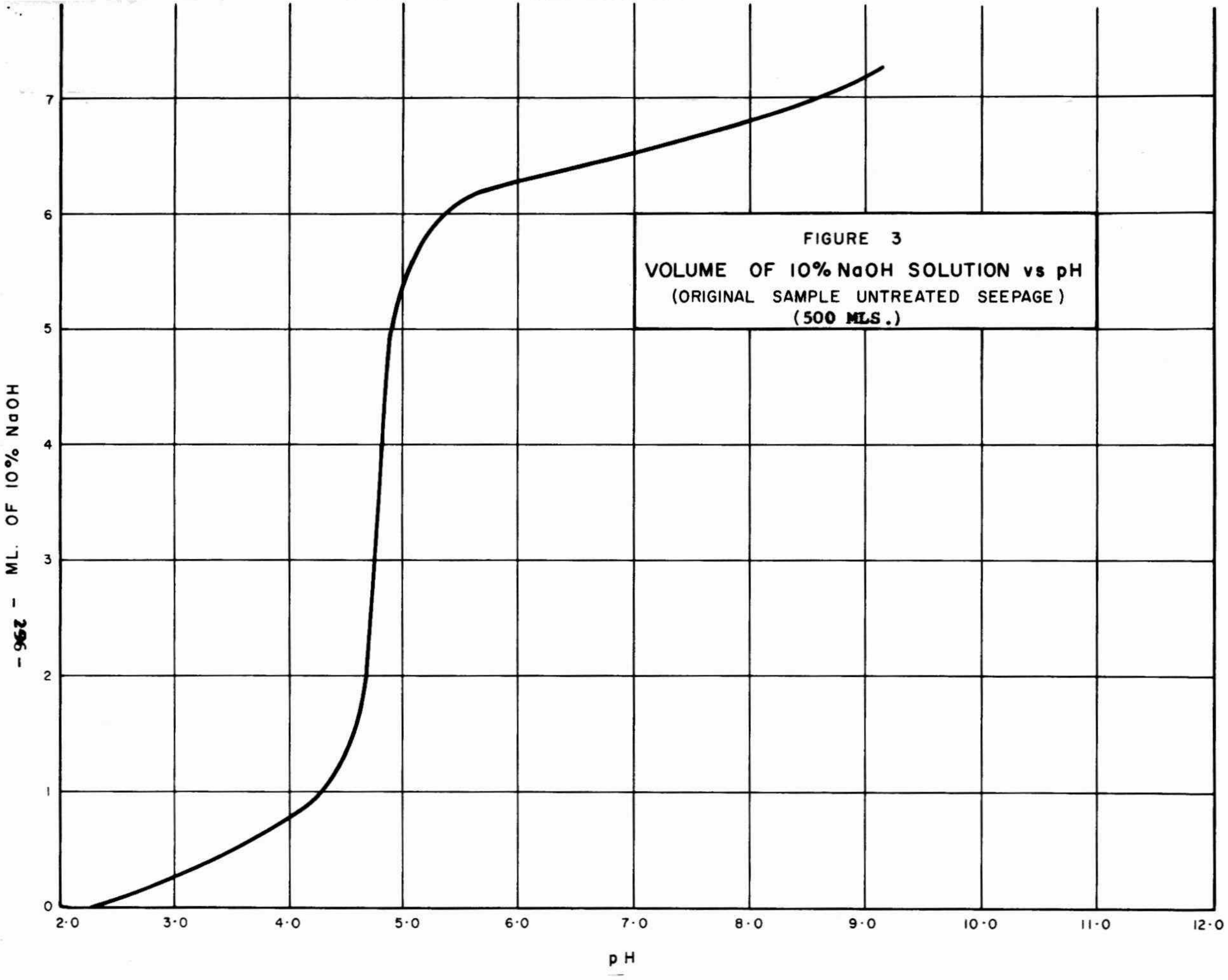


FIGURE 3

VOLUME OF 10% NaOH SOLUTION vs pH

(ORIGINAL SAMPLE UNTREATED SEEPAGE)

(500 MLS.)

quality standards can be met. However, any free acid that remains after metal precipitation still must be neutralized. The presence of a little free acid can cause a tremendous pH depression.

Natural ponding, inefficient as it may be, under the proper conditions will result in substantial reductions in metal and sulphate concentrations (effluent as opposed to influent). This, of course, represents a significant saving in neutralizing reagent costs.

Efficient ponding can be accomplished if the following conditions are satisfied:

(a) The retention time (the time the waste is held in the pond) must be as great as possible (in the order of months rather than days).

(b) The pond should be as shallow as possible (to enhance oxygen transfer from the atmosphere).

(c) The pond waste should not be allowed to come into contact with tailings containing iron sulphides.

(d) Wastes being decanted from the pond should be taken from the pond surface (preferably a sluice type overflow, etc.). The surface film of the pond is the zone of maximum oxidation and should therefore contain less unoxidized material than the waste a foot or so below the surface.

This type of pretreatment facility can be set up easily on most mining properties. The overflow should be directed to the area that receives the main decant overflow. In a few cases, the residual alkalinity of the decant (providing, of course, that the decant itself is alkaline) may be all that is required for final seepage treatment. In most cases, however, routine chemical treatment and subsequent settling will have to be provided.

The trace heavy metals can respond dramatically to this type of pretreatment. Substantial concentration reductions in some cases have been noted. Again, it is necessary to stress that this type of pretreatment is designed for seepage flows and must not be carried out in contact with iron sulphide bearing tails.

Although all seepage flows on any particular property should be combined before final discharge, each individual flow can be treated by itself in any convenient (relatively dry) depression. The overflow from each depression should be directed to a common area where final treatment (if necessary) could take place.

Since acid mine drainage situations do generally not reach a peak until after the individual properties have been abandoned and since treatment must continue especially on abandoned properties, it is wise to avoid mechanical pumping wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

Reference for this section: "Advanced Inorganic Chemistry, A Comprehensive Text" by Cotton and Wilkinson.

THE HANDLING OF RAW SEEPAGE FLOWS

In acid mine drainage circumstances raw (untreated) seepage flows usually contain excessive quantities of both ferrous and ferric sulphate--especially when the pH drops below 4.0 (a common occurrence).

Actual examples of ferrous-ferric relationships in diverse (unrelated) acid seepage flows are as follows:

pH	Total Ferrous Iron as Fe (ppm)	Total Ferric Iron as Fe (ppm)
3.4	1,090	1,400
2.6	850	90
3.0	45	311
3.1	210	124
2.9	trace	134
2.6	760	715
2.6	134	156
3.1	45	22
3.3	670	980
2.1	670	850
2.2	728	682
2.5	1,830	4,000
2.4	1,010	513
1.8	1,830	570
3.0	220	427

The ferric ion can and does enter into an oxidation-reduction reaction with iron sulphide whereby the ferric ion 'backtriggers' the oxidation of further amounts of sulphuritic materials (iron sulphides, etc.) to the sulphate form thereby accelerating the acid-forming process:

$$Fe_2(SO_4)_3 + FeS_2 + H_2O \dashrightarrow 3FeSO_4 + 2S^o$$

$$S^o + 3O + H_2O \dashrightarrow H_2SO_4$$

As a result, untreated acid seepage (containing either ferrous or ferric ions) should never be returned to a tailings basin. This type of seepage should be collected and chemically treated (with lime to a minimum pH of 8.5). After treatment, the seepage waste can be returned to the tailings basin. Although the practice of returning treated waste to a tailings area is acceptable, it is still not advisable. Seepage flows are maintained, in part, by water ponding on the tailings area. Thus, by returning seepage (treated or untreated) to a tailings area the problem is aggravated.

Seepage flows should be directed to one point for treatment, treated, and then discharged either to the recycle system intake area or to the same watercourse that receives the bulk effluent from the property.

TAILINGS AREA DESIGN

Tailings areas must be designed to minimize environmental effects due to problems such as acid mine drainage. Some points to consider are as follows:

(a) A tailings area should be located as high in a watershed as possible. In other words, a tailings area should intercept as little uncontaminated natural runoff as possible.

(b) A tailings area should not be located in an existing lake basin or in a very wet swampy area. In fact, a tailings mass should not cover any significant continuously running source of uncontaminated water. If such a source is covered with reactive tailings, the uncontaminated water will become contaminated and, as such, the volume of waste that should be treated will have increased unnecessarily.

(c) Whenever and wherever possible, tailings dams should be impermeable. Impermeable dams do not give rise to contaminated seepage flows.

(d) All seepage flows from the bases of permeable dams should be collected for treatment. As such, a trench which acts to intercept seepage flows should be constructed parallel to and a short distance from the downstream side of all permeable dams on any specific property. The waste collected by each trench should be directed to a central treatment facility.

(e) Since acid mine drainage situations generally do not reach a peak until after the properties have been abandoned and since treatment should continue especially on abandoned properties, it is wise to avoid mechanical pumping facilities whenever and wherever possible. A gravity flow which, on occasion, is more expensive to install at the outset, will be more economical in the long run.

(f) A tailings area decant should always be located as close as possible to the mill. Since waste treatment facilities will generally be located at or near a tailings area decant, a decant treatment facility close to the mill will:

- (i) permit shorter hydro lines to the site
- (ii) permit shorter access roads to the site and will hence reduce road construction and maintenance costs
- (iii) permit shorter water recycle, etc., lines from the site to the mill. Subsequent savings will be realized in pumping costs, insulation costs, etc.
- (iv) in some cases, permit waste treatment reagent storage tanks, mixing tanks, etc., to be located in the mill itself. Under these circumstances, waste treatment reagents could be pumped directly to the treatment area thus

eliminating the expense of a heated and automatically controlled waste treatment building at the treatment site itself.

(v) increase the chances of early detection by mine-mill personnel of any major waste treatment problems (excess turbidity, etc.).

(g) Generally speaking, a tailings area itself should not be regarded as a chemical waste treatment facility. Instead, the tailings area decant (plus all tailings area seepage) should be directed to a chemical waste treatment facility. In a few cases, the chemical waste treatment facility required may, of necessity, be somewhat elaborate. In most cases, however, the facility might consist of nothing more than two or three formal ponds of various sizes that are operated in series. The total industrial effluent (after solids removal in the tailings area) would enter the first pond. It is here that any required chemical additions would be made. The second pond, fed by the first, would then act as a settling basin and would retain any precipitate that was initiated in the first pond. The third pond might act as an alternate second pond to permit, when required, the cleaning (sludge removal) of the original second pond. On the other hand, the third pond, fed by the second pond, might be used as a source of recycle water or as a final effluent polishing pond (for final pH adjustment, etc.).

Note: It is very difficult to control the pH of a tailings area decant by neutralizing reagent additions in the mill itself. The very size of an average tailings area indicates the lack of response that may be expected at the decant point as a result of varying the quantity of neutralizing reagent additions in the mill. Also, the extremely high suspended solids content of most mill discharges to a tailings area must, by processes such as adsorption, reduce the effectiveness of any such neutralizing reagent additions. The required final pH range at the decant may be acquired by greatly over-neutralizing the waste stream in the mill but this is an expensive process and it tends to unduly increase the concentration of total dissolved solids in the final effluent from the property. pH control for waste treatment purposes should always be carried out at the point of decant overflow from the property. In this way, reagent additions (and reagent addition costs) are minimized. Increases in the concentration of total dissolved solids in the final effluent are also kept to a minimum.

(h) Wherever and whenever possible, tailings dams and related structures should be completed to their projected final height before milling commences at any specific property. All such structures should be immediately revegetated.

(i) Wherever and whenever possible, the revegetation of the surface of a tailings area should take place as soon as an area or a portion of an area is abandoned.

REVEGETATION

The stabilization of abandoned mine tailings areas in the Province of Ontario is now mandatory under the provisions of The Mining Act.

A well-developed continuous cover of vegetation on abandoned tailings areas and on the downstream slopes of all dams will ensure, to some degree, regulation of the effects of natural precipitation. Runoff, for all intents and purposes, will be eliminated. The volume of some seepage flows will be significantly reduced. The effects of the wind will be negligible. The area will blend into the surrounding landscape.

NOTE: In the sulphide mining district of Ontario, natural precipitation can theoretically account for up to 2,000 imperial gallons of seepage per acre per day.

The effectiveness of a well-developed cover of vegetation may be illustrated by the following:

(a) a single corn plant transpires at an average rate of 4 lbs. of water per day throughout its life of three or four months. One acre of corn loses approximately 8,400 gallons of water per day or between half to three-quarters of a million gallons during a life of two to three months.

(b) a twenty-year old spruce (twenty feet high) will transpire up to 100 gallons of water per day.

In essence, the revegetation of abandoned tailings areas minimizes the following problems:

(a) water pollution arising from the leaching of soluble matter in the tailings mass. Soluble matter is transferred from a tailings mass to a watercourse via seepage flows.

(b) erosion of impoundment structures. The erosion of tailings dams and dykes, etc., by either water or wind can result in massive tailings spills.

(c) air pollution arising from the blowing of fine dust. If the dust is chemically reactive, water pollution problems can also result.

(d) aesthetic pollution arising from the presence of sandy piles of waste material in an otherwise primitive or natural setting.

NOTE: A well-developed continuous cover of vegetation does not preclude the possibility of seepage flows from the area. If contaminated seepage flows still exist after revegetation, chemical treatment should be provided.

The successful establishment of a vegetative cover on an abandoned tailings area depends primarily on two major factors:

(1) the climatic conditions of the immediate area; and

(2) the chemical and physical characteristics of the tailings mass itself.

At present, the climatic factor cannot be modified to any great extent but must be taken into account when the choice of plant species for the area is made. In many cases, a tailings area is raised above the surrounding landscape and, as such, is exposed to the full force of the wind (from all directions), the full force of driving rains, and is unshielded from the sun.

Where young plants are concerned, the harsh climate of the sulphide mining district of Ontario is duplicated in only a few areas of the world. During the cool wet spring, the surface of an abandoned tailings area may be saturated with water. The summer, not uncommonly, brings daily temperatures of 100°F to the immediate surface of the tailings mass. The surface layers of the mass expand and contract with the result that delicate plant tissues are sheared and crushed. It is during the summer months primarily that masses of toxic efflorescent salts appear at or near the surface of the tailings area. The winter months present temperatures below -40°F in most areas. The tailings mass may be coated with several feet of ice and snow.

The mineralogical and/or chemical composition of any particular tailings mass is of prime importance where an attempt at revegetation is to be made. The chemical characteristics of a tailings mass are directly related to the chemical characteristics of the ore being recovered, the method of mining being employed, the type of mill circuit being utilized and the products being recovered. No two tailings areas have identical chemical compositions.

The following represent the partial chemical compositions (dry weight basis) of specific tailings masses in the Province of Ontario:

Case #1 (an iron operation)

Cobalt as Co	.0026%
Copper as Cu	.028%
Iron as Fe	13.1%
Lead as Pb	.020%
Manganese as Mn	.021%
Phosphate as PO_4	.08%
Potassium as K	.32%
Sodium as Na	.020%
Zinc as Zn	.021%

Case #2 (a gold operation)

Arsenic as As	11.7 ppm
Calcium as Ca	1.39%
Cyanide as HCN	1 to 35 ppm
Iron as Fe	1.69%
Phosphate as PO_4	.08%
Potassium as K	.022%
Sodium as Na	.012%

Case #3 (a uranium operation)

Cadmium as Cd	1.57 ppm
Cobalt as Co	14.2 ppm
Copper as Cu	37.8 ppm
Iron as Fe	12, 900 ppm
Lead as Pb	69.3 ppm
Manganese as Mn	10.4 ppm
Nickel as Ni	15.7 ppm
Phosphorus as P	.017%
Potassium as K	.25%
Sodium as Na	46 ppm
Zinc as Zn	4.10 ppm

Case #4 (a copper, lead, zinc operation)

Antimony as Sb	less than 30 ppm
Cadmium as Cd	18.0 ppm
Calcium as Ca	1,420 ppm
Cobalt as Co	35 ppm
Copper as Cu	803 ppm
Iron as Fe	20%
Lead as Pb	110 ppm
Manganese as Mn	218 ppm
Nickel as Ni	15.3 ppm
Phosphorus as P	25 ppm
Potassium as K	.18%

Sodium as Na	.04%
Zinc as Zn	3,900 ppm

Tailings areas that do not contain quantities of iron sulphide minerals can, in a relative sense, be easily revegetated. The sequence of events on such an area, in order to achieve revegetation, is as follows:

Apart from the steep side slopes, tailings piles are normally flat on top and little or no grading is necessary.

Underdrainage is not normally required since the top foot or so of tailings is generally fairly dry.

The first step in preparation for seeding is to break the hard crust which often forms on the surface of a tailings mass.

The surface is scarred to a depth of from 2 to 3 inches and the pH is adjusted, if necessary, by the application of lime or limestone, etc.

When the correct pH value is achieved, fertilizer is applied in an amount indicated by a chemical analysis of the tailings material. This rate of application is typically from 500 to 800 lbs./acre. A good compound fertilizer of the N:P:K (Nitrogen, Phosphorus, Potassium) type is generally required.

After the fertilizer has been applied, the seed is sown at a rate of between 50 to 150 lbs./acre. This rate is considerably higher than that used for a normally fertile area. Although the percentage germination will not be less than normal, the percentage reaching maturity may be considerably less.

After seeding, the area is lightly rolled and water is supplied if necessary.

Under normal circumstances the best time for sowing grass is at the end of summer, but with tailings areas practice has been to sow as soon as possible after the spring thaw. Various types of grass have been found to be suitable, several examples being:

Timothy (especially the variety S.48)
Creeping Red Fescue (and several other fescues)
Perennial Rye Grass
Reed Canary Grass

Among the legumes which must be sown with the grass are:

Crown Vetch
Birdsfoot Trefoil

and the clovers,

Early Red Clover
White Clover

It has been found that a mixture of different grasses gives better results than a seeding of a single type.

After seeding, a period of intensive management is required to ensure that by the end of summer a strong cover is obtained. Thin or bare patches may then be reseeded.

It should be noted that subsequent applications of fertilizer should be based on the "little but often" plan, since much of the fertilizer will be carried below the growth region by applied or natural water.

By the end of the second growing season, the plants should be well established and apart from an occasional application of fertilizer, the cover crop should be self-supporting.

Although trees have been successfully grown directly in tailings, they require almost constant maintenance and it may be expected that as much as 50% of the saplings will die and will have to be replaced. Much better results have been had with trees after the establishment of a strong grass cover.

Tailings areas that contain quantities of iron sulphide minerals can, with difficulty, be revegetated. The main problem, of course, is that the iron sulphide minerals in the tailings mass, over a period of time, break down to release water soluble, acid-producing salts that are definitely toxic to most common forms of vegetation. In addition, these salts tend to migrate into the surface layers of a tailings mass and become concentrated there.

The migration of unwanted toxic salts to the surface of an abandoned tailings area can be arrested by the application of even a thin layer of coarse waste rock or gravel over the surface of the tailings area. Since most of the toxic salts migrate to the surface of a tailings mass via capillary action, the large spaces between the coarse waste rock (or gravel) fragments act as an effective barrier to the migration. Although it is possible to induce a vegetative growth on bare rock, a thin layer of soil (even very poor quality soil) spread over the waste rock layer will virtually ensure conditions that are conducive to plant growth.

A variation of the above scheme to achieve revegetation, but perhaps not quite as effective, is to practice (iron) sulphide removal at a mill late in the life of an operation. A two or three foot final layer of sulphide-free tails (over pre-existing sulphide tails) would, in effect, convert the problem of revegetation of the area to a problem of the non-sulphide area type (which can be solved with relative ease).

In some instances, an ore will give rise to tailings containing enough carbonate-type minerals so that all acid produced by sulphides in the tailings mass is neutralized in situ and, as a result, most toxic salts are precipitated in situ. It is necessary to stress, however, that cases of this type are quite rare.

If the tailings mass contains significant quantities of iron sulphide minerals and if

(a) waste rock and soil are not to be spread over the surface of the tailings mass;

(b) sulphide recovery will not be practiced in order to produce at least a sulphide-free surface layer on the tailings mass; and

(c) the ore does not generate tailings with sufficient residual neutralizing power to control all acid that could be produced in the tailings mass

then a neutralizing agent such as limestone or lime must be thoroughly mixed into the surface layers of the tailings mass in order to achieve an environment that is suitable for plant growth. If not enough neutralizing agent is added to the surface layers of the tailings mass, a good initial vegetative cover could be achieved followed by an overall 'kill' of vegetation. The 'kill' would be due to the depletion of the neutralizing reagent reserve that was present in the surface layers when revegetation procedures commenced and when neutralizing reagent additions were made. It is apparent that sulphide reactions will continue to generate acid in the tailings mass in zones beneath the zone of neutralizing reagent addition. For this reason more than any other, it appears that permanent, self-maintaining revegetation based on neutralizing reagent additions alone is not impossible but is highly uncertain.

The initial neutralization of the upper few inches of an acid tailings area prior to seeding can be accomplished with powdered lime or finely-divided limestone or a mixture of both. The residual alkalinity can be attained and maintained with a graded limestone product.

Limestone tends to be quite expensive in the mining districts of Ontario simply because the mining camps are frequently to be found considerable distances from the limestone producing centres in southern Ontario.

It should be emphasized that the limestone required for maintaining alkalinity in the upper layers of a pyritic tailings area need not be pure. Quite often the limestone can be found in sedimentary strata, sedimentary outliers, or metamorphic equivalents of carbonate sediments within a reasonable trucking distance of the mining operations. Gravel deposits that have been derived by glaciation from the aforementioned often contain significant quantities of carbonate pebbles. Pit-run or screened gravel is much cheaper than crushed limestone.

Wherever and whenever possible, tailings areas should be revegetated with plant species that are native to the area. In most cases, however, a strong (and generally non-native) grass or legume cover must be established on an area before native species can be introduced. It is always a good idea to look for and identify all species of vegetation that have been naturally established on a tailings area before revegetation attempts begin. A single stunted plant growing by itself in the middle of a three hundred acre tailings area may provide an invaluable clue as to which types of vegetation will survive and which will not survive after a grass cover has been established.

Whenever and wherever possible, acid-tolerant species of vegetation should be used to revegetate a sulphide-bearing tailings mass.

Although it is generally recognized that the introduction of organic material (rotted leaves, hay, wood fibre, animal manure, black muck, peat, etc.) is invaluable with regard to the establishment of vegetation on a barren tailings mass, sludge from a municipal sewage plant should be used with a degree of caution.

The sludge from a municipal treatment plant often contains appreciable quantities of metals. Chromium, zinc, copper and nickel are routinely encountered. It is possible that these metals could end up in area watercourses.

Plants, responsive to their environment, exhibit the ability to pick up and concentrate metals. In this sense, it is doubtful that any vegetation grown on a mine tailings area should be distributed for use or used by humans or farm animals. With regard to the foregoing, one should be extremely cautions concerning the disposal of any vegetation that is grown on a tailings mass containing radioactive compounds.

ADVANCED MINE WASTE TREATMENT METHODS

Rapidly advancing technology in the fields of biology and water resources management indicates that, in general, waste control systems (including lime treatment) presently being used by the mining industry are not capable of producing final effluents of a quality that will satisfactorily ensure the protection of fish and other aquatic life.

In general, all waste treatment systems that are presently being efficiently used and operated by the mining industry result in effluents that contain small but still undesirable concentrations of metals and non-metals. Furthermore, the use of most, if not all, of these systems results in a substantial increase in the total dissolved solids concentration in the effluents from the systems.

In general, the natural background concentrations of metals in watercourses in mining areas tends to be abnormally high. Therefore, it is possible that environmental regulatory agencies will, in the future, require essentially 'no discharge' of specific substances (particularly specific metals) in mining areas where a particular substance is a problem.

New approaches are currently needed to counter existing and future mine-mill waste treatment problems. As waste treatment systems, of necessity, become more complex they also become more expensive. Therefore, in order to keep costs down, wastewater recycle should be considered as an inherent part of any approach to mine-mill waste treatment. Wastewater recycle acts to reduce the total volume of effluent from a property and, as such, permits the installation of smaller and more efficient treatment plants.

Advanced waste treatment systems can be designed on the basis of many technical concepts. Some of these concepts are as follows:

(i) distillation and/or evaporation
(ii) crystallization or freezing
(iii) reverse osmosis
(iv) solvent extraction
(v) electrodialysis
(vi) adsorption
(vii) liquid extraction
(viii) ion exchange
(ix) biological systems

Of the above, three concepts have received the most attention. These concepts are:

(1) ion exchange

(2) electrodialysis

(3) reverse osmosis

Basic comments concerning the above three were given in a paper entitled "Polishing of Base Metal Mine Effluents by Advanced Treatment Methods" by V. Kresta of the New Brunswick Water Authority in Fredericton, New Brunswick.

The comments are as follows:

(1) Ion Exchange

Besides water softening and demineralization, one of the major fields of application of ion exchange has been and is likely to continue to be in the recovery of valuable metals from solutions and in the treatment of wastewaters. Most of the literature concerns the recovery of metal ions from acidic solutions. Cation exchangers operating in the hydrogen ion exchange cycle, that are regenerated with acids, are employed for this purpose in hydrometallurgy, treatment of pickling wastes, dilute leach liquors and acid coal mine drainage. The treatment of tailings pond effluents from base metal mines represents a different situation: they are generally alkaline in reaction and the value of metals to be removed is irrelevant due to their extremely low concentration. No economic benefit from the metal recovery can be expected.

The present day sulfonated resins, i.e., the strongly acidic cation exchangers such as the sulfonated styrene co-polymers, possess rather high capacities which are not influenced by the pH of the solution treated; the capacity for copper is virtually constant between pH 2 and pH 12. They are, however, not selective enough with respect to members of a group of ions. For bivalent ions the increase in affinity has been established to be as follows:

$$\mathrm{Cd} < \mathrm{Be} < \mathrm{Mn} < \mathrm{Mg} = \mathrm{Zn} < \mathrm{Cu} = \mathrm{Ni} < \mathrm{Co} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Pb} < \mathrm{Ba}$$

The differences in affinity are, however, rather small. Thus, no selective separation can be achieved. The interfering substances consume acid during elution, equivalent for equivalent or somewhat more, and consequently these ion exchangers are less suitable than those possessing carboxylic groups.

Carboxylic acid cation exchangers are ineffective below pH 4, but offer high exchange capacity at high pH and an efficient utilization of acid regenerant. It has been stated that an extremely dilute solution of copper sulfate may be concentrated into a saturated solution of copper sulfate by passage over the sodium salt of a carboxylic acid exchange resin and subsequent elution with 10 per cent sulfuric acid. Because of its peculiar nature, a carboxylic cation exchange resin exhibits unusual selectivity in both, the adsorption and elution phases of the cycle. Experience has shown that simple carboxylics are quite selective for the copper ion even in the presence of large concentrations of sodium, calcium and magnesium. The unusual affinity of the carboxylic acid group for divalent ions is related undoubtedly to the low acidity of the group. The covalent bonds of the carboxylic group with hydrogen ions warrants the assumption that the carboxylic group forms covalent bonds with other ions capable of forming covalent bonds. Copper has a much greater ability to form covalent bonds than calcium. Carboxylic acids should, therefore, be capable of selecting copper over calcium with much higher efficiency than sulfonic acid resins. Measurements of the interactions of a polymetacrylic acid - divinylbenzene copolymer with Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ca^{2+} indicated that the metal complex equilibrium constants increased in the order

$$Ca^{++} < Ni^{++} < Zn^{++} < Cu^{++} < Fe^{+++}$$

The high difference in selectivity of the resin for copper and zinc over calcium allows for the following equations:

$$Cu^{++} + CaR \rightleftarrows CuR + Ca^{++}$$

$$Zn^{++} + CaR \rightleftarrows ZnR + Ca^{++}$$

Another researcher assumed the following approximate values of equilibrium constants in the polycarboxylic system (Amberlite IRC - 50)

$$K_{Ca^{++}}^{Cu^{++}} = \frac{CuR}{CaR} \cdot \frac{Ca^{++}}{Cu^{++}} = 50 \qquad (1)$$

$$K_{Ca^{++}}^{Zn^{++}} = \frac{ZnR}{CaR} \cdot \frac{Ca^{++}}{Zn^{++}} = 10 \qquad (2)$$

Thus, the affinity of Amberlite IRC - 50 for Cu^{++}

is 50 times that for Ca^{++}, and similarly, the affinity for Zn^{++} is 10 times that for Ca^{++}. This is favourable. However, ferric ions will be bound much more strongly than either copper or zinc ions whereas ferrous ions will be somewhat less absorbed relative to these ions. It is possible that organic compounds used as flotation aids in a mine-mill circuit may influence the performance and lifetime of the resin.

(2) Electrodialysis

Electrodialysis has the advantage in that the operational costs are almost directly related to the amount of salt removed. The process offers therefore an economic advantage for treatment of waters with low total dissolved solids concentrations. Extensive research done in this field has shown that divalent ions transfer in preference to monovalent ions. The electrodialysis process would therefore also seem to hold promise as a method of removing copper and zinc from mine wastewaters. However, several problems arise when applying the elctrodialysis technique to this type of waste. First of all, partial separation of all ions occurs upon electrodialysis. The driving force for ion removal is an electrical field applied across the membrane. Since the transport number of any ion in a phase is proportional to the product of its concentration and its mobility, the transport number of an ion in an ion selective membrane phase is governed by both these quantities as they occur in the membrane. In the electrodialytic demineralization of natural waters using ion selective membranes, it was often found that heavy metal ions present in low concentrations in the water were readily absorbed and retained by the cation selective membranes, and consequently such ions accumulated in the membrane. In the presence of monovalent ions, this feature is known as poisoning of the membrane. Some special technique would have to be developed to make use of this feature when treating mine wastewaters.

Another problem is the high resistance at low total dissolved solids concentrations. Values much below 500 ppm give impractically high figures, and this value is normally the limit to which the electrodialysis process is taken. The high resistance of the electrolyte at low concentrations can be countered by filling the dialysate compartment of the unit with a mixed bed of strongly dissociated ion exchange resin. By this means, the concentration range over which electrodialysis is feasible can be extended, since the electrical conductivity of a dilute electrolyte solution in the presence of a mixed bed of ion exchange resin is largely that of the resin itself. The major limitation of this technique is the onset of hydrolysis of the resin if exchangeable ions are removed from it at a greater rate than they are replaced by the solution.

Another problem is the occurrence of high levels of calcium sulphate in many mine wastewaters. Under these circumstances, any attempt to increase the efficiency of electrodialysis can lead to super-saturation with subsequent deposition of calcium sulfate throughout the cell. The resultant scale would be extremely difficult to remove. In desalination of brackish water this problem is somewhat reduced by the fact that the solubility of calcium sulfate rises with increasing sodium chloride concentration. Nevertheless, the necessity for avoiding saturation is permanent, and the ratio of concentrated/diluted stream flow rates must always be set so as to make it impossible to exceed saturation in the cell. In mine wastewaters, the beneficial effect of a high concentration of common salt on the solubility of calcium sulphate is generally absent. Unless measures are applied to reduce the calcium ion concentration in the feed, the ratio of concentrated/diluted stream flow rates is likely to be very unfavourable.

Finally, there is a problem of the overall performance reliability including cell re-assembly after cleaning. A membrane cell consists essentially of several hundred fairly soft plastic sheets, separated by an equal number of plastic spacers, all of which must be assembled together in the correct order, with exact alignment of the ports. There is no difficulty in carrying out this task in a factory producing membrane cells. However, this is not the case when the cells are used in remote areas where servicing must be carried out by general fitters. This appears to be one of the reasons why the electrodialysis technique, which in the early 1950's appeared the most promising method for brackish water treatment, has not fulfilled early expectations.

Today's experience with electrodialysis is based on fairly small units. A tailings area decant treatment unit without mine-mill wastewater recycle would generally have to be very large. The only very large pilot program, in the Orange Free State, South Africa, using the biggest block of cells assembled anywhere in the world, was finally closed because technical difficulties rendered the technique less attractive than other methods.

(3) Reverse Osmosis

The reverse osmosis technique could give reliable results in the treatment of mine wastewaters. The equipment is not complicated and is easily automated. The method, which essentially consists of removal of salts by filtering them away from water under pressure, is appealing in its simplicity. This method is being favoured at present for many reasons. Possibly the most cogent is the recent development of membranes which combine good salt rejection with reasonable pressures. Another reason is the low consumption of chemicals. The pH, however, must be maintained between 5 and 6.5 to avoid hydrolysis of the membranes which would reduce their life. A high rejection of heavy metals might be expected since there is no selectivity in ion removal. The main drawbacks are the very high investment costs and the comparatively high operating costs due to the relatively short life of the membranes, usually between 3 and 4 years. With mine wastewaters, two more drawbacks must be considered.

(1) The volume of rejected water (concentrate) which must be recycled is likely to be high in order to avoid precipitation of calcium sulfate.

(2) The low temperature of the water to be treated adversely affects the process.

It has been stated that the recovery might not be greater than 75 percent if the content of calcium sulfate in the feed is about 50 percent of saturation. This, unfortunately, is a common situation. Also, with regard to temperature, it appears that up to 80 percent more modules would be required at 35°F to produce the same amount of 'water' generated by a unit operating at 68°F.

Of all of the processes discussed, ion exchange appears to be the most promising. However, it is extremely doubtful that any of the major and less expensive advanced methods of mine waste treatment could be presently economically employed without first:

(a) reducing the volume of waste to be treated. This can be accomplished via mine-mill wastewater recycle.

(b) removing to acceptable levels, by chemical treatment, etc., substances that could cause fouling of the advanced treatment system.

TAILINGS DAM SEALANTS

One of the most interesting materials that is available for use as a tailings structure sealant and seepage control agent is a naturally occurring clay known as bentonite.

Bentonite is a clay that is characterized by an ability to swell 10 to 15 times its original volume when in contact with moisture. The predominant clay mineral in bentonite is montmorillonite. However, in reality, montmorillonite itself is a group of clay minerals whose formulas may be derived by substitution in the general formula $Al_2Si_4O_{10}(OH)_2$ with deficiencies in charge in the tetrahedral and octahedral positions balanced by the presence of cations, most commonly Ca and Na, subject to ion exchange. Representative members of the group are:

montmorillonite	$Na_{.33}(Al_{1.67}Mg_{.33})Si_4O_{10}(OH)_2$
nontronite	$Na_{.83}(Fe^{+3}_{2.00})(Al_{.33}Si_{3.67})O_{10}(OH)_2$
saponite	$Ca_{.17}(Mg_{3.00})(Al_{.83}Si_{3.67})O_{10}(OH)_2$
hectorite	$Na_{.33}(Mg_{2.67}Li_{.33})Si_4O_{10}(F,OH)_2$
sauconite	$Ca_{.12}Na_{.09}(Zn_{2.40}Mg_{.18}Al_{.22}Fe^{+3}Al_{.53}Si_{3.47})O_{10}(OH)_2$
stevensite	$Ca_{.15}Mg_3Si_4O_{10}(OH)_2$

There are two general types of bentonite recognized. These are:

(a) the sodium or high-swelling type such as is found in Wyoming; and

(b) the calcium or low-swelling type that is found in Texas, California, Mississippi, Greece, Australia and Yugoslavia (this material swells to only 1 or 2 times its original volume).

At the present time, bentonite is used in the pelletizing of iron ore concentrates, sealing of reservoirs, as a plasticizing agent in paints, as a paper filler, as a clarifying agent of wine, as a carrier in cosmetics and pharmaceuticals, and in the production of high quality iron castings.

Bentonite is generally shipped from Wyoming, U.S.A., as a minus 200 mesh powder and as a 'crude' product containing bentonite fragments varying from 1/8 inch to ¼ inch in diameter.

A ½ to 1 inch thick layer of bentonite applied to the entire upstream face of a tailings dam could possibly seal a dam. It can be applied dry and then simply wetted. When wet, it forms a sticky impermeable seal that can cling to almost any surface. It does not decompose, is nontoxic, and appears to be unaffected by wet-dry and freeze-thaw cycles.

Suggested uses of bentonite are:

(a) to effectively seal tailings dams

(b) to stop or reduce seepage from existing dams (i.e., apply the crude or powdered bentonite as a slurry or as a dry material to the upstream regions -- suckerholes, etc., -- of seepage origin).

(c) to effectively seal the surface layers of a tailings area and thus prevent the upward migration of the acid salts that tend to kill vegetation. Surface runoff should be uncontaminated.

NOTE: Vegetation cannot easily penetrate the bentonite layer. As such, if a bentonite layer has been applied to the surface of a tailings area that is to be revegetated, a thin layer of soil or tailings should be applied on top of the bentonite.

Bentonite essentially requires no storage sheds or cover of any type. It forms its own surface seal that repels water.

It appears that bentonite, powder or 'crude', could be used to counter or minimize seepage flows in many of the situations that arise in the mining industry.

Many materials, other than bentonite, have been suggested for use as tailings dam sealants in order to prevent the escape of contaminated seepage flows from tailings areas. The materials in question include synthetic organic polymers and inorganic salts. Information concerning these materials is generally readily available from the major chemical processors and suppliers.

MISCELLANEOUS

(1) Effects of Naturally Occurring Chelating Agents

Many streams are known to contain significant quantities of natural chelating agents such as humic compounds. It is possible that these substances act to reduce the toxic effect of metals and, as a result, may account for the existence of fish in waters that contain what are thought to be lethal levels of metals. The literature on this particular subject is sparse.

(2) Effects of Increased Water Hardness

In general, the toxic effect of metals decreases with increasing water hardness.

(3) Underground Disposal of Tailings, Pyrite, Etc.

At many underground mining operations, the coarse fraction of the tailings is recovered in the mill and then sent underground as a structural support material (backfill). Substances such as cement can be (and frequently are) added to the coarse tailings fraction in order to increase the underground strength of the final mass. However, since fine grinding is generally needed to liberate mineral values from an ore, the coarse tailings fraction in most cases makes up only a small percentage of the total volume of tailings produced in a mill. As such, in most cases, the use of backfill in underground operations does not significantly reduce the area requirements for a tailings basin.

It is also necessary to point out that tailings generally occupy a much greater volume than does the ore from which the tailings were derived. The exception, of course, is when the ore is extremely high grade. Since tailings do occupy a greater volume than ore-in-place, it would be difficult and is presently impossible to return to the underground workings all tailings produced at an operation.

In many cases, it appears that iron sulphide concentrates could be directed to underground mined-out areas for storage.

(4) Nutritional Requirements of Mine Water Micro-Organisms

In order to achieve maximal bacterial activity in mine-mill discharge waters, it is obviously necessary that adequate concentrations of required nutrients be present. Oxygen, carbon dioxide, nitrogen, phosphorus, ferrous iron and sulphate are nutrients that must be present in significant amounts. It has been stated that between 1 and 10 mg/litre ammonium ion is required to support microbial oxidation of 800 mg/litre ferrous iron. Nitrate or nitrite can serve as the nitrogen source. It has also been stated that between 0.55 and 5.5 mg/litre of phosphate is needed to support microbial oxidation of 9,000 mg/litre ferrous iron.

It may be significant that the most serious cases of acid mine drainage in the Province of Ontario occur in a mining camp (Elliot Lake, Ontario) in which mills are characterized by their heavy usage of sulphuric acid, ammonia and nitrate.

Explosive substances (containing ammonium nitrate, etc.) used at nearly all mining operations probably do contribute to the overall nutrient problem at an operation.

(5) Reactions of Naturally Occurring Simple Sulphides

(a) Copper Sulphides

(oxidation mechanism)

$Cu_2S \dashrightarrow CuS + Cu^{++} + 2e$

$CuS \dashrightarrow Cu^{++} + S + 2e$

NOTE: Chalcocite Cu_2S (see section #9 "The Sulphides and Sulphosalts")

Covellite CuS (see section #28 "The Sulphides and Sulphosalts")

Cupric hydroxide gradually changes to the more stable CuO with time.

When an alkali hydroxide is added, a cupric sulphate solution precipitates antlerite $Cu_3(OH)_4SO_4$ and brochantite $Cu_4(OH)_6SO_4$.

(b) Lead Sulphide

$PbS \dashrightarrow Pb^{++} + S + 2e$ (acid solution)

$PbS + 2H_2O \dashrightarrow Pb(OH)_2 + S + 2H^+ + 2e$ (neutral to moderately basic solution)

The sulphate ion precipitates the plumbous ion in solution as white lead sulphate (anglesite) when the activity product of the two ions exceeds the solubility product of lead sulphate.

The lead sulphate dissociates as follows:

$$PbSO_4 \dashrightarrow Pb^{++} + SO_4^{=},\ K = (Pb^{++})(SO_4^{=}) = 1.3 \times 10^{-8}$$

NOTE: Galena PbS (see section #13 "The Sulphides and Sulphosalts")

The general reaction

$MeS \dashrightarrow Me^{++} + S + 2e$ (Me = metal) is also known to be operative in the cases of MnS and CoS.

(6) pH

The negative logarithm of the hydrogen ion activity is the theoretical definition of pH. In practice, pH is defined by the approximate relation

$$pH = -\log_{10} \left[H^+ \right]$$

It is measured by a pH meter usually using the calomel-glass electrode system. Although pH is a useful parameter in assessing the quality of mine water, it does not establish the true pollutional potential of a water. The following data relate pH to sulfuric acid acidity:

pH	Acidity as H_2SO_4, ppm	pH	Acidity as H_2SO_4, ppm
2	490	5	0.49
3	49	6	0.049
4	4.9	7	0.0049

The accurate measurement of pH in the field is complicated by the many variables affecting the measurement such as temperature, variability of composition, and dissolved gases.

(7) Total Acidity

Total acidity is defined as the amount of standard base required to titrate a sample of mine water to pH 8.3 after removal of dissolved CO_2. The total acidity does not indicate the acid condition, i.e., the $\left[H^+\right]$ of the mine water, but reflects the potential total quantity of $\left[H^+\right]$ which is liberated during the oxidation and hydrolysis of various cations in solution. For example,

$$Fe^{+2} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ + e$$

represents the overall reaction involved in the oxidation of ferrous iron to ferric iron and the subsequent hydrolysis of the Fe^{+3} ion. Al^{+3} and Mn^{+2} are two other mine water components which contribute to acidity. The relative acidity of each of the mine water constituents is as follows:

H^+ 1 ppm of H^+ = 49 ppm of acidity as H_2SO_4

Fe^{+2} 1 ppm of Fe^{+2} = 1.75 ppm of acidity as H_2SO_4

Fe^{+3} 1 ppm of Fe^{+3} = 2.625 ppm of acidity as H_2SO_4

Al^{+3} 1 ppm of Al^{+3} = 5.44 ppm of acidity as H_2SO_4

Mn^{+2} 1 ppm of Mn^{+2} = 1.78 ppm of acidity as H_2SO_4

(8) It is probable that various minerals, particularly the sulphide minerals, act like metals in galvanic combinations. That is, when two sulphide minerals are in contact in a tailings area, etc., one sulphide may accelerate or retard the (electrochemical) decomposition of the other sulphide.

It has been experimentally shown that the oxidation rates of most sulphides increase when dissimilar sulphides are intimately mixed.

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